CHAPTER IV

TEST RESULTS AND DISCUSSIONS

4.1 Foundry sand selection

In phase 1 of the study, leachability test results, percent zinc removal of foundry sand from the batch experiment, and the particle size distribution curves were used as the criteria to select suitable foundry sand for the column experiment.

From the leachability test results in Table 4.1 it can be concluded that there were only a small amount of heavy metals contained in the leachate from each of the waste foundry sands. In addition, Barium (Ba), Cadmium (Cd), and Cromium (Cr) were found in the leachate of foundry sand from Siam Magotaux Co., Ltd. Both Ba and Cr were also found in the leachate of foundry sand from Siam Nava Industry Co., Ltd., whereas only Ba was found in leachate of foundry sand from Siam Navaloha Foundry Co., Ltd., and Asian Autopart Co., Ltd. Waste foundry sand leachate metal contents were however well below the USEPA and PCD industrial effluent standard. As a result, waste foundry sands were considered as non-hazardous waste. This suggests that using waste foundry sand as a media to treat wastewater will not make the water to be more hazardous. From this section Siam Nava Industry foundry sand was chosen to do the column experiment.

Table 4.1 The leachability test results of foundry sand

Metal	Siam Magotaux Co., Ltd. (mg/l)	Siam Nava Industry Co., Ltd.(mg/l)	Siam Navaloha Foundry Co., Ltd.(mg/l)	Asian Autopart Co., Ltd.(mg/l)	USEPA and PCD Standard (mg/l)
As	<0.05	<0.05	<0.05	<0.05	5
Ba	1.451	0.511	0.682	0.494	100
Cd	0.025	<0.005	<0.005	<0.005	1
Cr	<1.442	0.004	<0.007	<0.007	5
Pb	<0.050	<0.050	<0.050	<0.050	5
Hg	<0.040	<0.040	<0.040	<0.040	0.2
Se	<0.050	<0.050	<0.050	<0.050	1
Ag	<0.007	<0.007	<0.007	<0.007	5

Available from: Thunsiri (2004)

Table 4.2 Percent of Zn removal of foundry sands

Media	Percent of zinc removal (%)
Siam Magotaux Co., Ltd.	79.04
Siam Nava Industry Co., Ltd.	84.77
Siam Navaloha Foundry Co., Ltd.	76.04
Asian Autopart Co., Ltd.	58.74

Available from: Thunsiri (2004)

According to the batch experimental results in Table 4.2, foundry sand from Siam Nava Industry Co., Ltd. had the highest percentage of Zn removal, followed by foundry sand from Siam Magotaux Co., Ltd., Siam Navaloha Foundry Co., Ltd., and Asian Autopart Co., Ltd. respectively. It can therefore be inferred that foundry sand from Siam Nava Industry Co., Ltd. can remove the highest amount of zinc from contaminated water and was thus chosen as the suitable medium for the column experiment. Beside the capacity or the ability to remove zinc from wastewater, the medium that is used for industrial wastewater treatment is expected to have the ability to treat a lot of wastewater in a short time. In another words it should have high permeability. It Figure 4.1 showed that the foundry sand had high permeability.

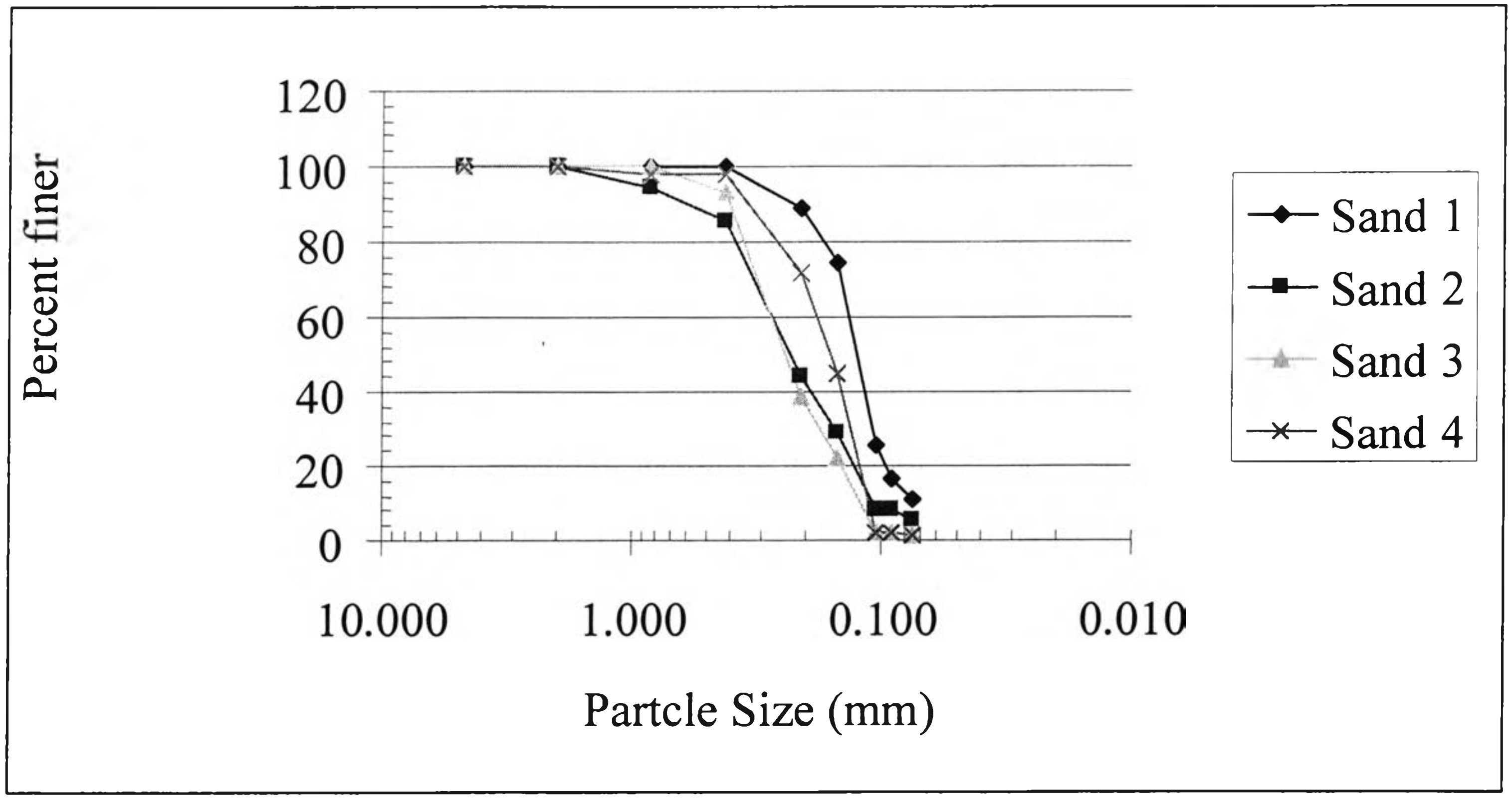

Figure 4.1 Particle size distribution curves for spent foundry sands.
Available from: Thunsiri (2004)
Note: Sand 1-4 stand for foundry sand from Siam Magotaux Co., Ltd., Siam Nava Industry Co., Ltd., Siam Navaloha Foundry Co., Ltd., and Asian Autopart Co., Ltd., respectively.

These foundry sands contained a small clay fraction as it was used as a binder in foundry molding processes. The percent of fine particle (fraction passing the US no. 200 sieve, 75μm) ranges from 1.35% (foundry sand Asian Autopart Co., Ltd.) to 11.28% (foundry sand from Siam Magotaux Co., Ltd.), and clay fraction ranges from 0% (foundry sand Asian Autopart Co., Ltd.) to 19.14% (foundry sand from Siam Magotaux Co., Ltd.).

According to the results from preliminary experiment, foundry sand collected from Siam Nava Industry Co., Ltd., had high permeability. The leachability test carried out also proved that the foundry sand was not hazardous. It can therefore be affirmed that foundry sand from Siam Nava Industry Co., Ltd. was the most appropriate foundry sand for the "column experiment".

4.2 Column experiment

Based on the results from phase 1, foundry sand from Siam Nava Industry Co., Ltd. was chosen as the medium in the column experiment. In this phase, conditions were varied in order to investigate the effects of specified parameters on column performance. The results were displayed in a graph to show the tendency of data such as tendency of pH and elements concentration in the samples at different period.

The comparison graphs showed the zinc breakthrough curve at different conditions. The curve was plotted between the porevolume versus the concentration of zinc which was shown as a ratio of Ce/Co (the concentration of effluent over concentration of influent) to yield the maximum value of 1.

The objective of the study was to find which parameter can affect the foundry sands capacity, and the breakthrough time or the amount of zinc that was removed in the same period of time. Five parameters were studied.

4.2.1 Effect of bed height

To observe the difference in column performance at varying bed heights.

Table 4.3 Parameters and their designated values under which varying bed heights were monitored.

Parameters	Values
Bed height	14.5, 18, 21.5, and 25 cm
Flow rate	6 ml/min
Initial concentration	60 mg/l
pH	5
Column operation mode	Up-flow

The effluent history showed the typical 'S' shape of a packed bed system (Figure 4.2, 4.3, 4.4 and 4.5). The zinc concentration in the effluent was at first under the detectable limit of the inductively couple plasma (0.2 μg/l). At a porevolume of 120, 110, 80 and 40 and bed height 25, 21.5, 18 and 14.5 cm respectively, the concentration sharply rose until it was equal to the influent concentration thereafter, the column became exhausted and the concentration of zinc became stable. In contrast, Ca concentration was initially stable at concentration of 36.43, 45, 41, 41 mg/l and bed height of 14.5, 18, 21.5 and 25 cm respectively). The concentration however, started to decrease at about the same time when zinc concentration began to increase; that is at 30, 70, 110 and 110 min and bed height of 14.5, 18, 21.5 and 25 cm respectively). The concentration became stable at the same time as the zinc. The results thus implied that a relationship perhaps exist between Zn and Ca. The breakthrough time, at a bed height of 14.5 cm, showed that this height was almost the minimum height of column at flow rate 6 ml/min, pH 5, initial concentration 60 mg/l, and up-flow mode. A shorter bed height may cause breakthrough immediately at start of the experiment.

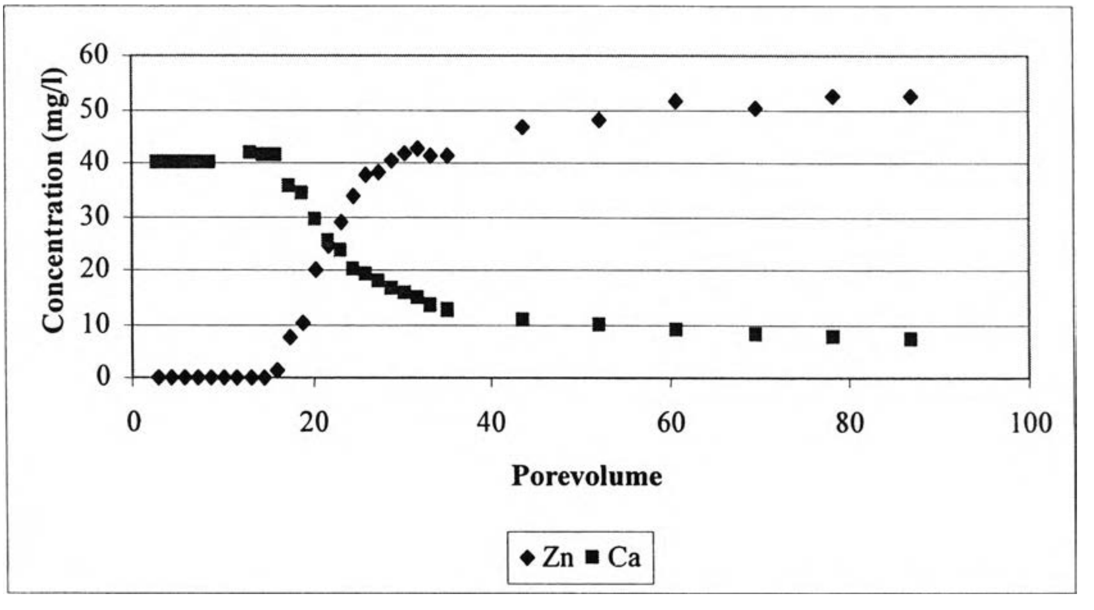

Figure 4.2 Elements concentration in the samples under the following conditions: bed 25 cm, flow 6 ml/min, conc. 60 mg/l, pH 5, up-flow

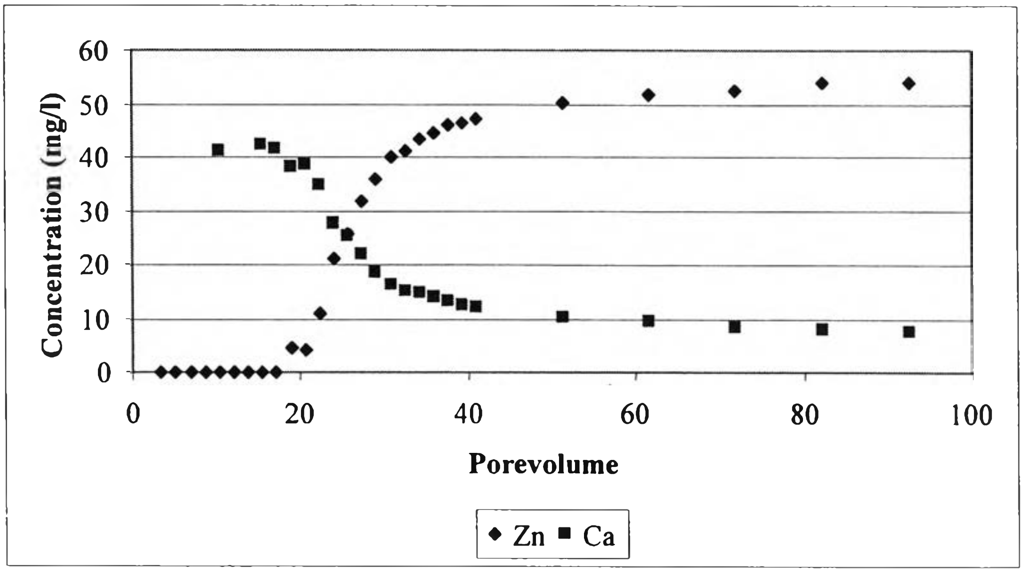

Figure 4.3 Elements concentration in the samples under the following conditions: bed 21.5 cm, flow 6 ml/min, conc. 60 mg/l, pH 5, up-flow

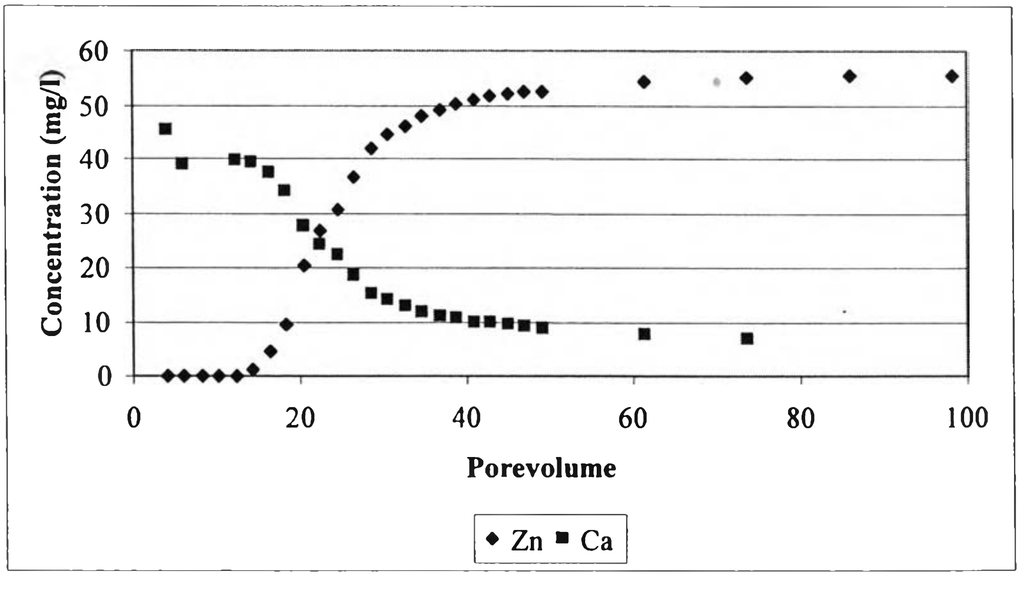

Figure 4.4 Elements concentration in the samples under the following conditions: bed 18 cm, flow 6 ml/min, conc. 60 mg/l, pH 5, up-flow

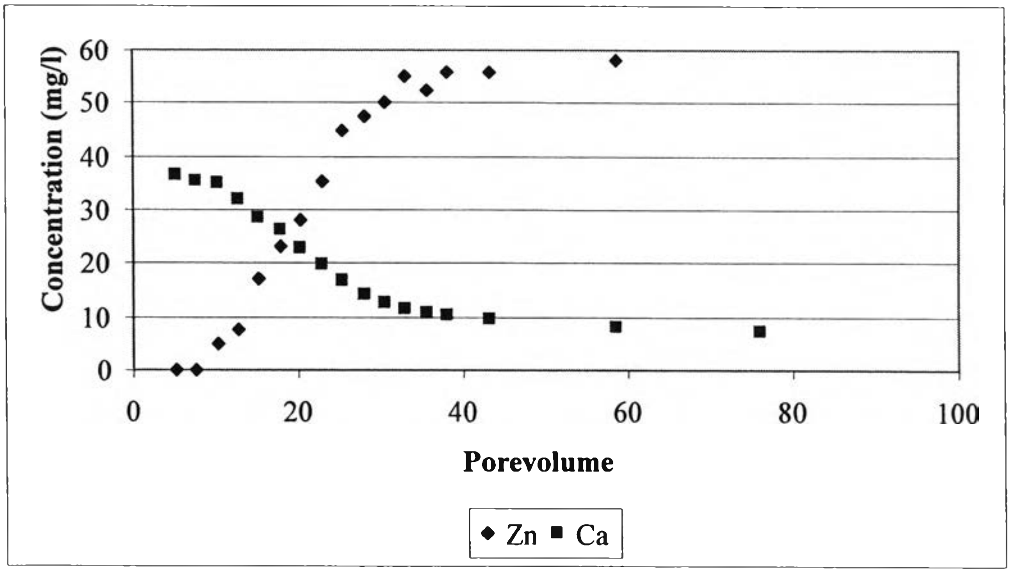

Figure 4.5 Elements concentration in the samples under the following conditions: bed 14.5 cm, flow 6 ml/min, conc. 60 mg/l, pH 5, up-flow

Figure 4.6-4.9 showed the results of pH and substances concentration in samples at different bed heights and different porevolumes. The vertical axis showed the pH value of the samples and the horizontal axis showed the porevolume values.

With regards to the tendency of the pH value (Figure 4.6, 4.7, 4.8 and 4.9); the first dot at porevolume zero indicated the initial pH value of the solution of influent reservoir to be close to pH 5. After the solution was passed through the column system, the pH values increased to around pH 7, thereafter decreased to pH 6 where it stabilized.

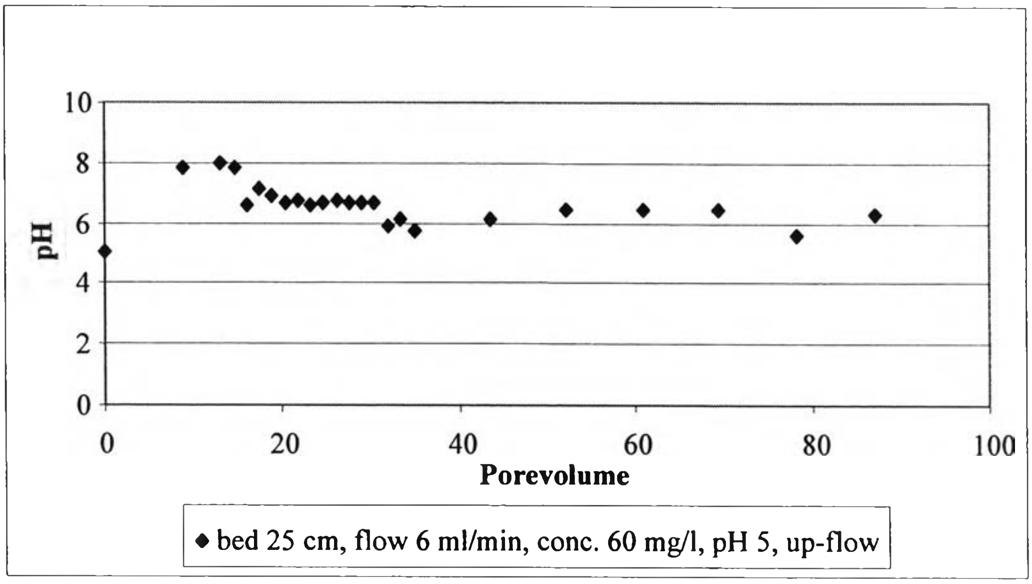

Figure 4.6 pH in the samples under the following conditions: bed 25 cm, flow 6 ml/min, conc. 60 mg/l, pH 5, up-flow

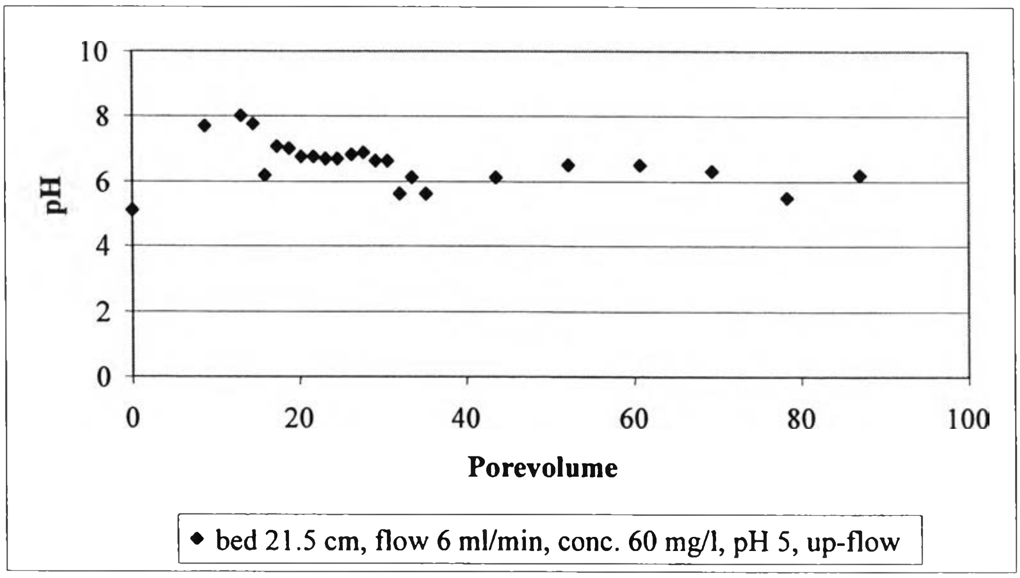

Figure 4.7 pH in the samples under the following conditions: bed 21.5 cm, flow 6 ml/min, conc. 60 mg/l, pH 5, up-flow

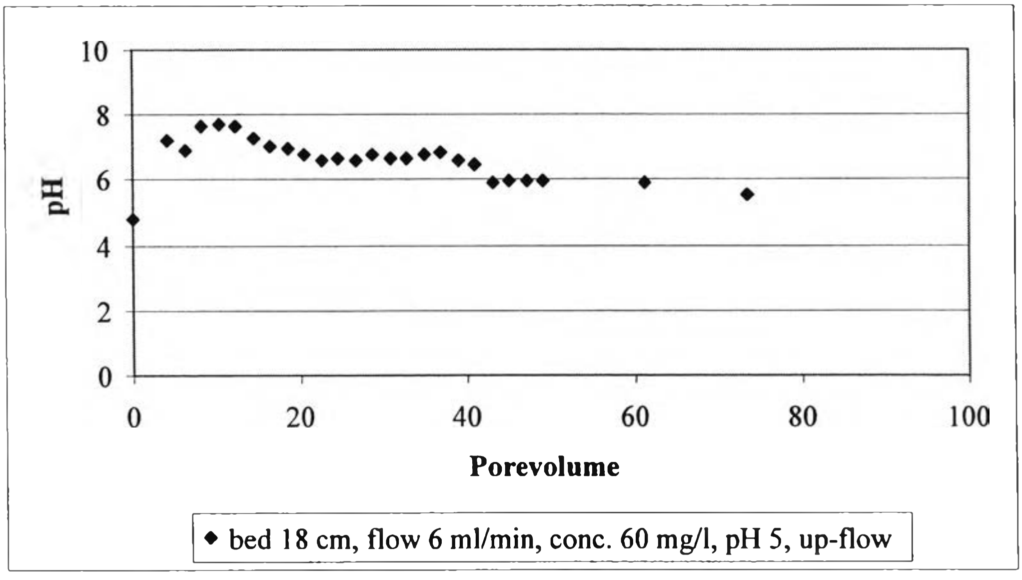

Figure 4.8 pH in the samples under the following conditions: bed 18 cm, flow 6 ml/min, conc. 60 mg/l, pH 5, up-flow

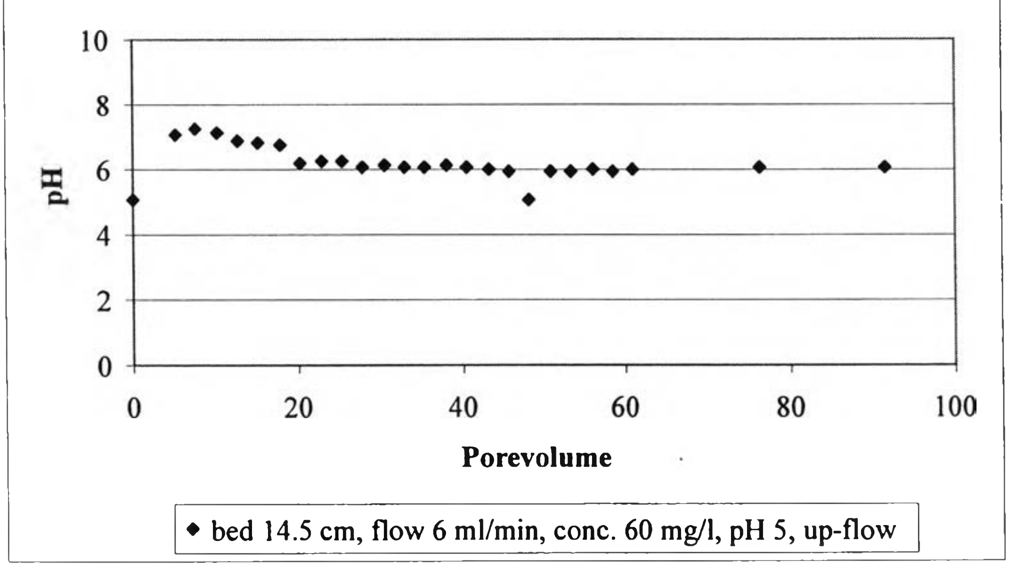

Figure 4.9 pH in the samples under the following conditions: bed 14.5 cm, flow 6 ml/min, conc. 60 mg/l, pH 5, up-flow

4.2.2 Effect of flow rate

To observe the difference in the column performance at varying flow rates.

Table 4.4 Parameters and their designated values under which varying flow rate were monitored.

Parameters	Values
Bed height	25 cm
Flow rate	6, 11 and 15 ml/min
Initial concentration	60 mg/l
pH	5
Column operation mode	Up-flow

The effluent history showed the typical 'S' shape of a packed bed system (Figure 4.10, 4.11, and 4.12). The zinc concentration in the effluent was at first under the detectable limit of the inductively couple plasma (0.2 μg/l). At a porevolume of 120, 60, and 50 and flow rate of 6, 11, and 15 ml/min respectively the concentration rose sharply until it became equal to the influent concentration. Thereafter, the column became exhausted and the concentration of zinc became stable. In contrast, the Ca concentration was initially at high levels of 40, 38, and 37 mg/l of flow rate 6, 11, and 15 ml/min, respectively. Thereafter the concentration started to decrease at the same time, the zinc concentration started to rise (110, 50, 40 min of flow rate 6, 11, and 15 ml/min, respectively), and they both became stable at the same time.

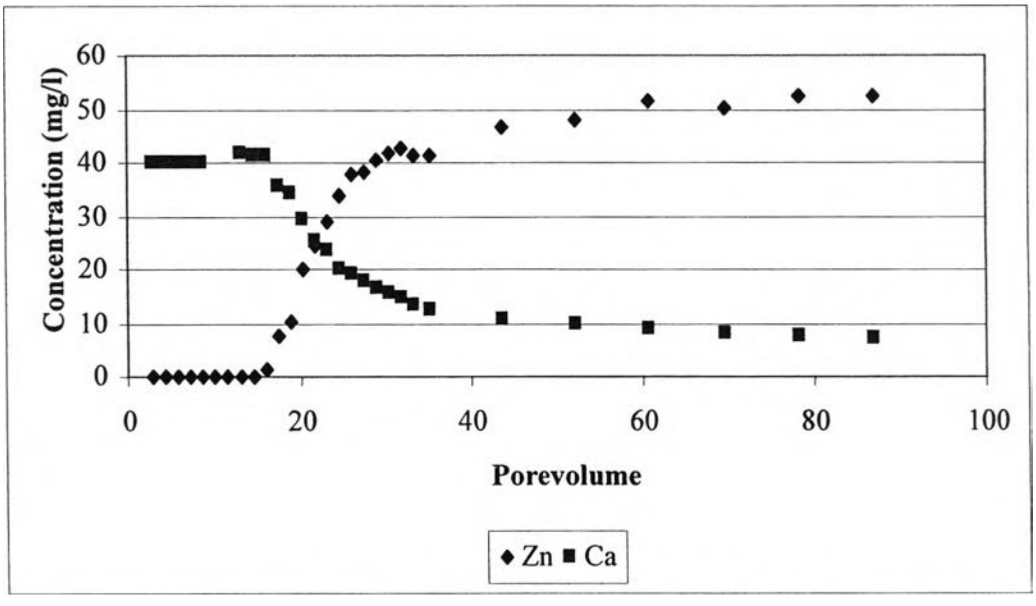

Figure 4.10 Elements concentration in the samples under the following conditions: bed 25 cm, flow 6 ml/min, conc. 60 mg/l, pH 5, up-flow

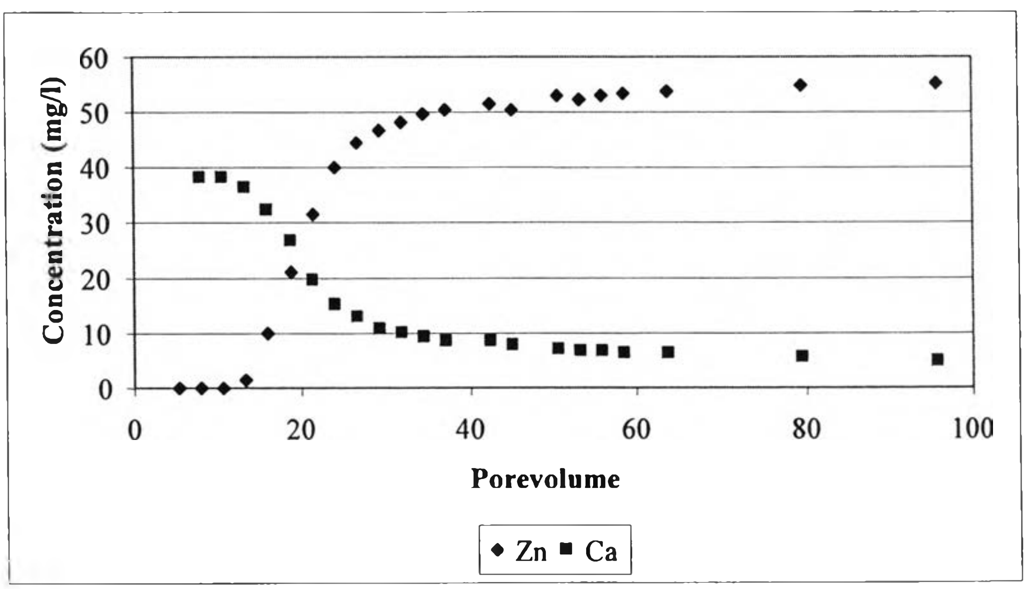

Figure 4.11 Elements concentration in the samples under the following conditions: bed 25 cm, flow 11 ml/min, conc. 60 mg/l, pH 5, up-flow

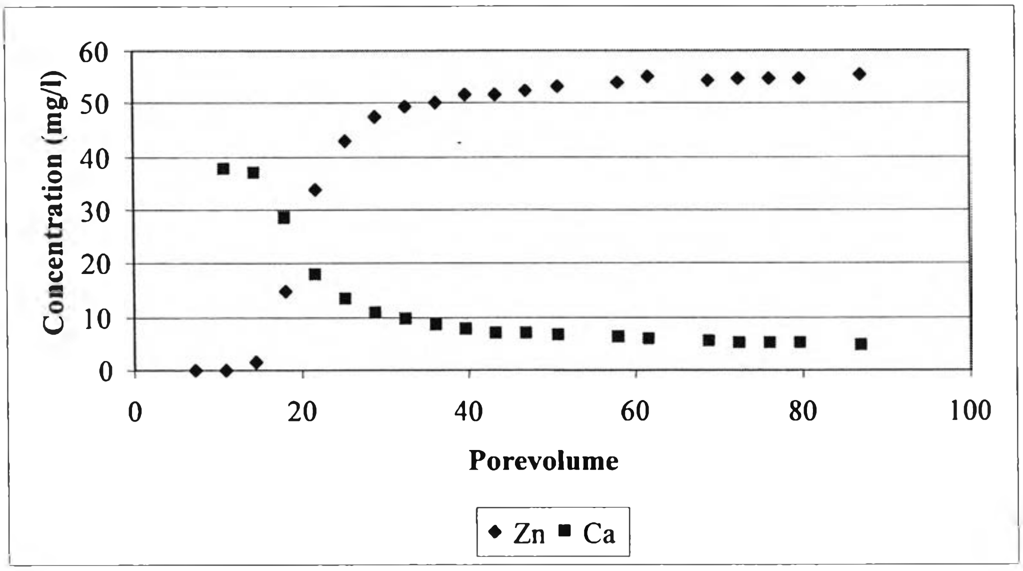

Figure 4.12 Elements concentration in the samples under the following conditions: bed 25 cm, flow 15 ml/min, conc. 60 mg/l, pH 5, up-flow

4.2.3 Effect of initial concentration

To observe the difference in column performance at varying initial influent concentrations.

Table 4.5 Parameters and their values used to monitor the effect of initial concentration.

Parameters	Values
Bed height	21.5 cm
Flow rate	6 ml/min
Initial concentration	30, 60 mg/l
pH	5
Column operation mode	Up-flow

The effluent history showed the typical 'S' shape of a packed bed system (Figure 4.13, and 4.14). The zinc concentration in the effluent was at first under the detectable limit of the inductively couple plasma (0.2 μg/l). The concentration then rose sharply until it became equal to the influent concentration. The column thereafter became exhausted, and thus stable. In contrast, the Ca concentration was initially stable at concentration of 21, and 40 mg/l with initial concentration at 30 and 60 mg/l, respectively. The concentration then started decreasing as the zinc concentration started rising at porevolume of 25.7 and 18.85 with initial concentration at 30 and 60 mg/l, respectively. They both became stable at the same time.

From Figure 4.13 and 4.14 it can be seen that initial concentration had an effect on the breakthrough time of the column. The initial concentration of 60 mg/l had a shorter breakthrough time than 30 mg/l.

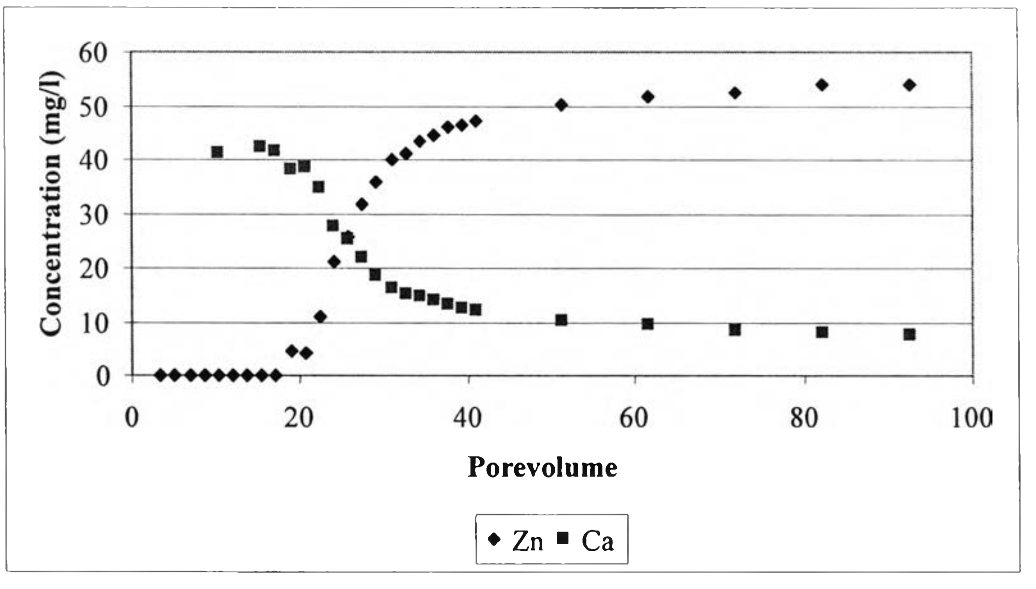

Figure 4.13 Elements concentration in the samples under the following conditions: bed 21.5 cm, flow 6 ml/min, conc. 60 mg/l, pH 5, up-flow

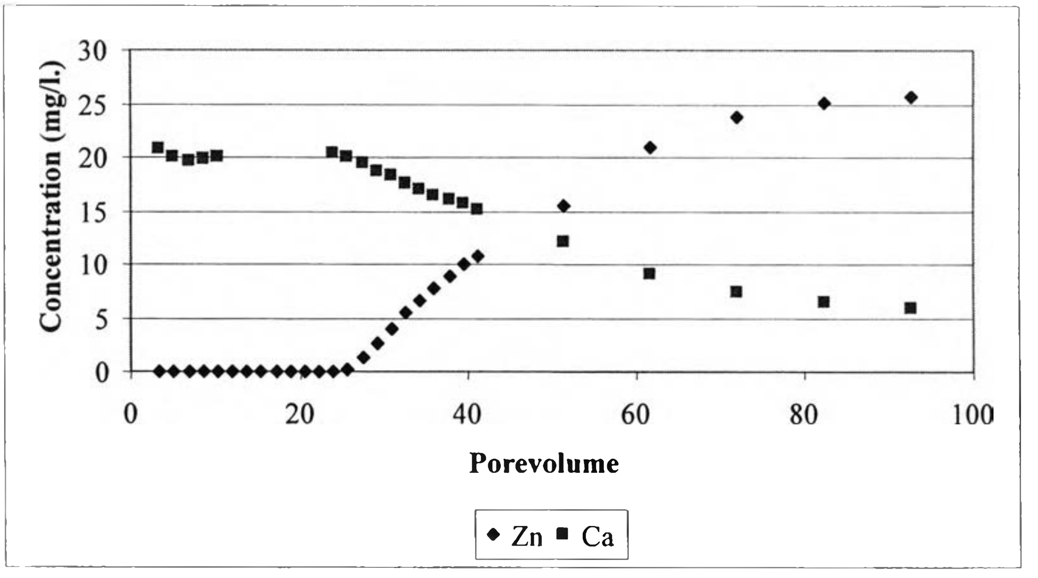

Figure 4.14 Elements concentration in the samples under the following conditions: bed 21.5 cm, flow 6 ml/min, conc. 30 mg/l, pH 5, up-flow

With regards to the tendency of the pH value (Figure 4.15 and 4.16); the first dot at porevolume zero indicated the initial pH value of the solution of influent reservoir was closed to pH 5. After the solution was passed through the column system, the value of the pH increased as much as pH 7 thereafter decreased to pH 6 where it stabilized.

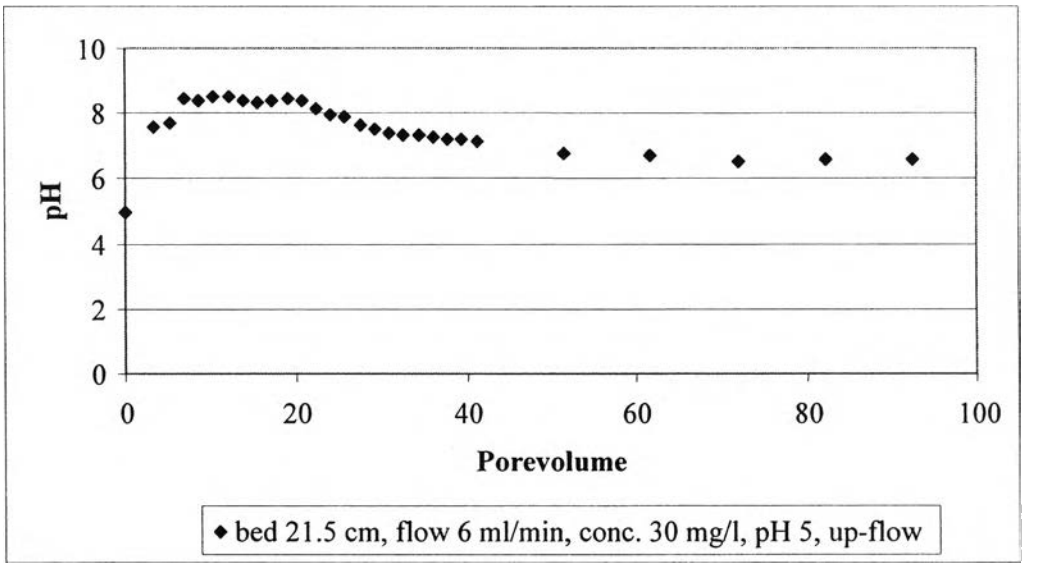

Figure 4.15 pH in the samples at the following conditions: bed 21.5 cm, flow 6 ml/min, conc. 30 mg/l, pH 5, up-flow

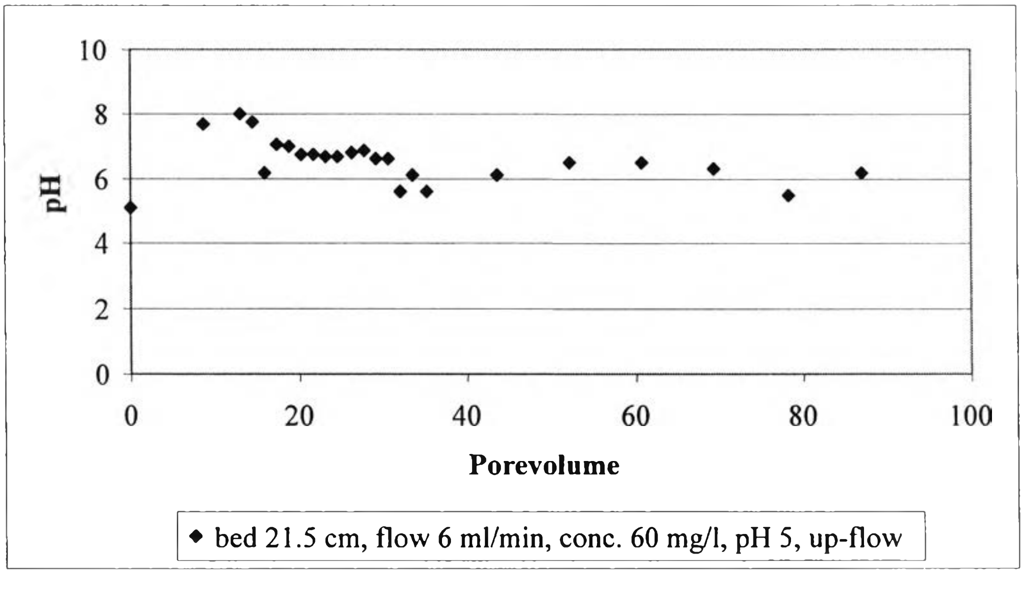

Figure 4.16 pH in the samples under the following conditions: bed 21.5 cm, flow 6 ml/min, conc. 60 mg/l, pH 5, up-flow

4.2.4 Effect of initial pH

To observe the difference in column performance at changed initial pH of the influent solution.

Table 4.6 Parameters and their values used to monitor the effect of initial pH.

Parameters	Values
Bed height	21.5 cm
Flow rate	6 ml/min
Initial concentration	60 mg/l
pH	3 and 5
column operation mode	Up-flow

The effluent history showed the typical 'S' shape of a packed bed system (Figure 4.17 and 4.18). The zinc concentration in the effluent was initially under the detectable limit of the inductively couple plasma (0.2 μg/l). At porevolume of 110 and 70 and pH 5 and 3 respectively the concentration then rose sharply until it became equal to the influent concentration and thus the column became exhausted and thereafter stable. In contrast, the Ca concentration was initially stable at concentration of 63 and 41 mg/l at pH 3 and 5, respectively. The concentration then started decreasing. At the same time the zinc concentration started rising (11 and 18.85 pore volume of pH 3 and 5, respectively) and both Zn and Ca became stable at the same time.

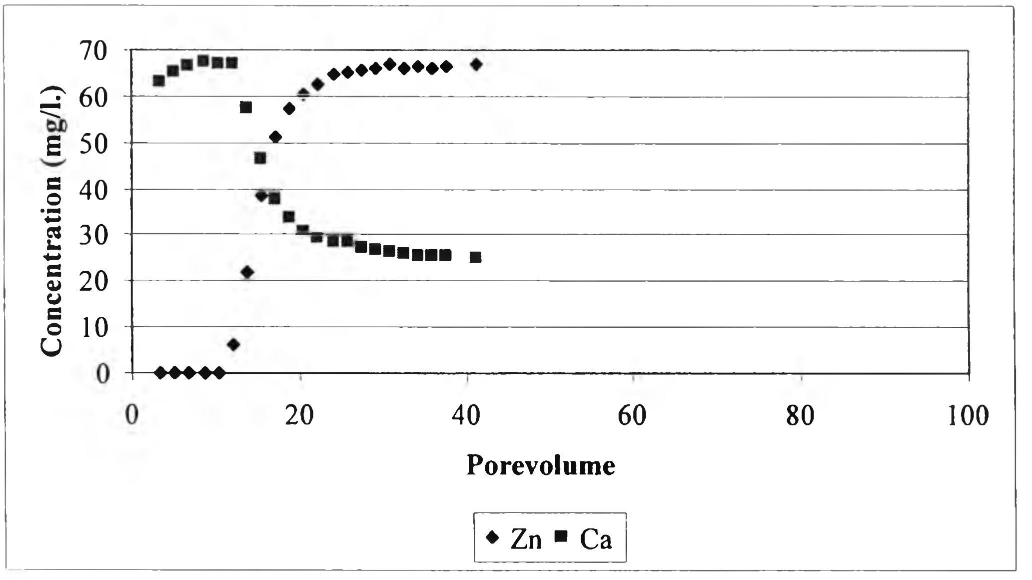

Figure 4.17 Elements concentration in the samples at the following conditions: bed 21.5 cm, flow 6 ml/min, conc. 65.5 mg/l, pH 3, up-flow

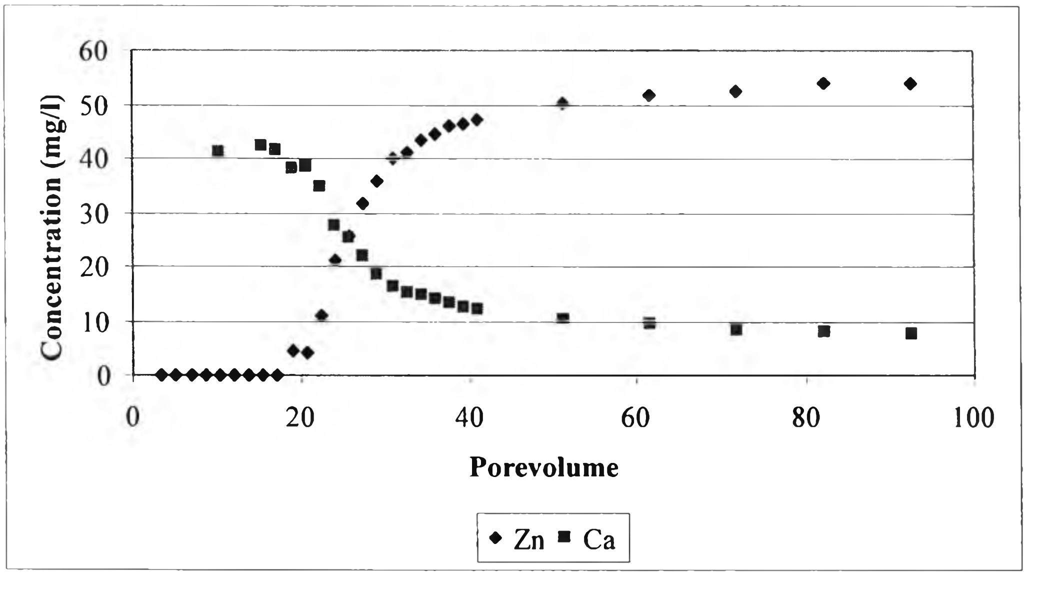

Figure 4.18 Elements concentration in the samples under the following conditions: bed 21.5 cm, flow 6 ml/min, conc. 60 mg/l, pH 5, up-flow

Figure 4.19 and 4.20 showed the result of pH and substances concentration in the samples at different bed heights and different porevolumes. The vertical axis showed the pH values and the horizontal axis showed the porevolume values.

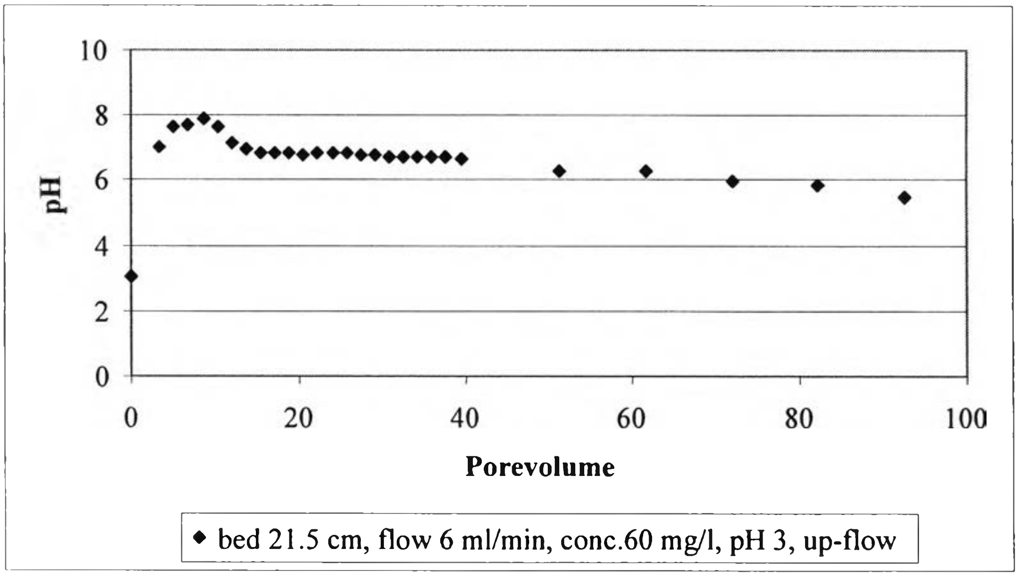

Figure 4.19 pH in the samples at the following conditions: bed 21.5 cm, flow 6 ml/min, conc. 65.5 mg/l, pH 3, up-flow

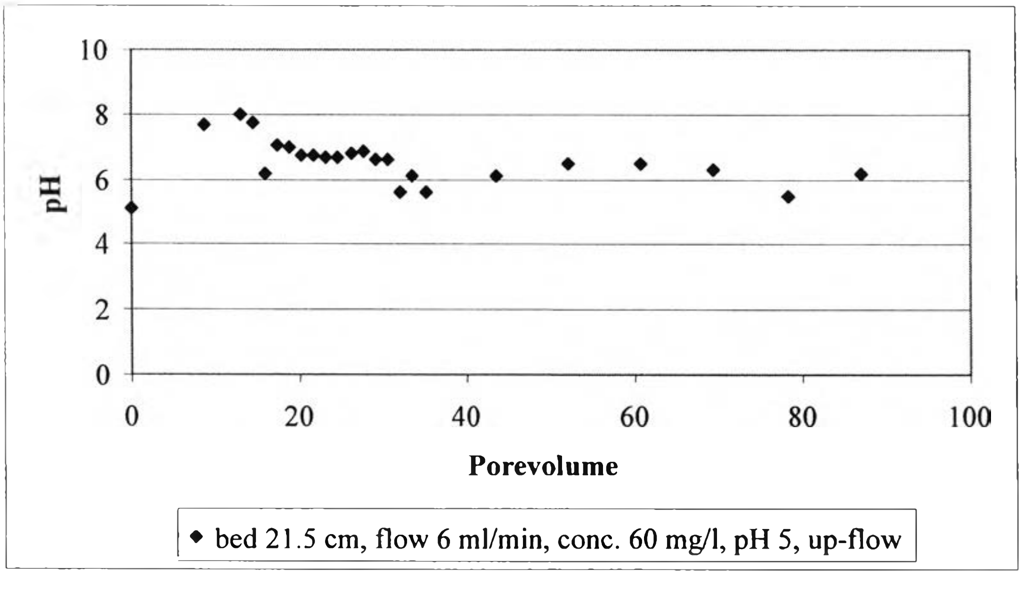

Figure 4.20 pH in the samples under the following conditions: bed 21.5 cm, flow 6 ml/min, conc. 60 mg/l, pH 5, up-flow

With regards to the tendency of the pH value (Figure 4.15 and 4.16); the first dot at porevolume zero indicated the initial pH of the solution of influent reservoir was closed to pH 5. After the solution was passed through the column system, the value of the pH increased about 7, thereafter decreased to pH 6 where it stabilized.

4.2.5 Effect of column operation modes

The objective of this part was to investigate the difference in column performance between two modes of column operation.

Table 4.7 Parameters and their values used to monitor the effect of column operation modes experiment.

Parameters	Values
Bed height	21.5 cm
Flow rate	6 ml/min
Initial concentration	60 mg/l
pH	5
Column operation mode	Up-flow and down-flow

The effluent history showed the typical 'S' shape of a packed bed system (Figure 4.21 and 4.22). The zinc concentration in the effluent was initially under the detectable limit of the inductively couple plasma (0.2 μg/l). At porevolume of 110 and 60 and mode up-flow and down-flow respectively the concentration then rose sharply until it became equal to the influent concentration and thus the column became exhausted and thereafter stable. In contrast, the Ca concentration was initially stable at concentration of 41 and 38 mg/l at up-flow and down-flow modes, respectively. The Ca concentration then started decreasing. At the same time, the zinc concentration started rising (20.56 and 12 pore volume of up-flow and down-flow, respectively), and both Ca and Zn concentration became stable at the same time.

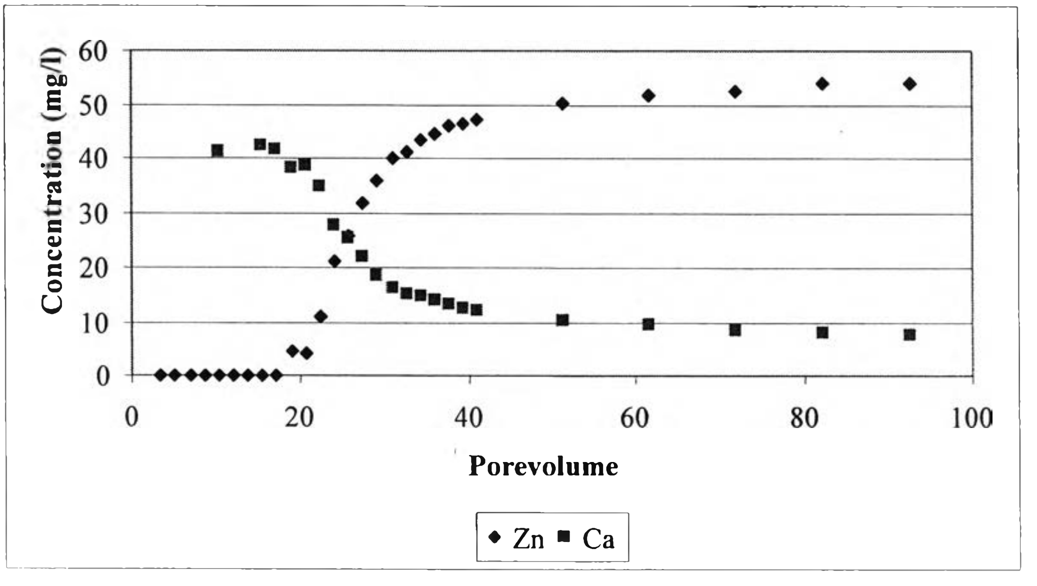

Figure 4.21 Elements concentration in the samples under the following conditions: bed 21.5 cm, flow 6 ml/min, conc. 60 mg/l, pH 5, up-flow

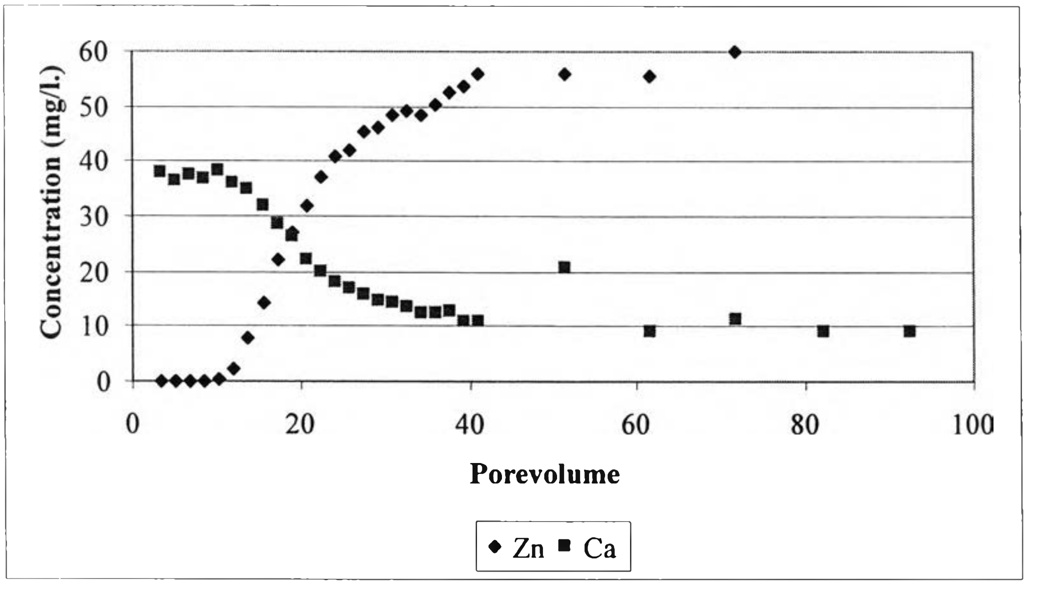

Figure 4.22 Elements concentration in the samples at the following conditions: bed 21.5 cm, flow 6 ml/min, conc. 60 mg/l, pH 5, down-flow

Figure 4.23 and 4.24 showed the result of pH and substances concentration in the samples at different bed heights and different porevolumes. The vertical axis showed the pH value and the horizontal axis showed the porevolume values.

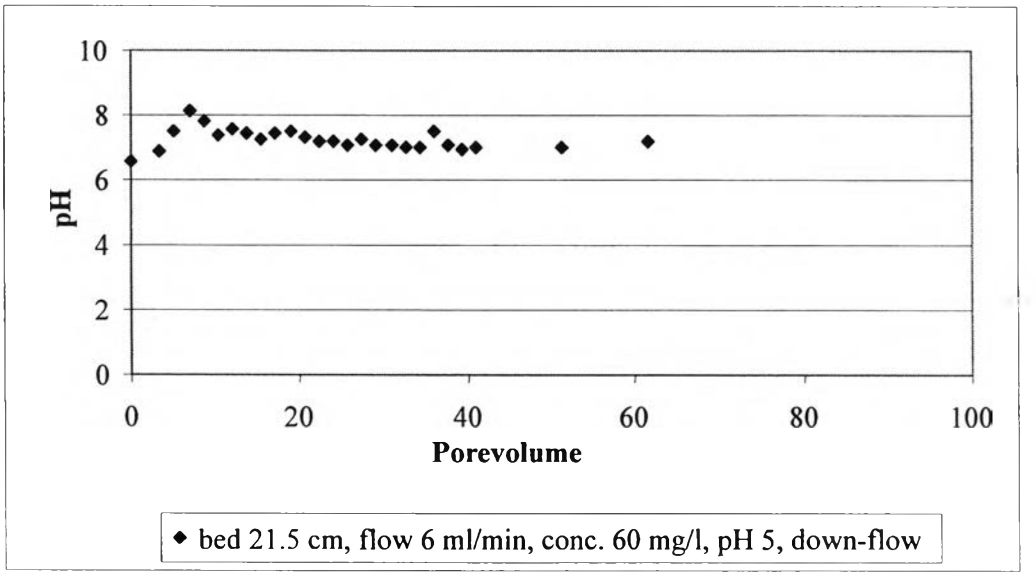

Figure 4.23 pH in the samples at the following conditions: bed 21.5 cm, flow 6 ml/min, conc. 60.0mg/l, pH 5, down-flow

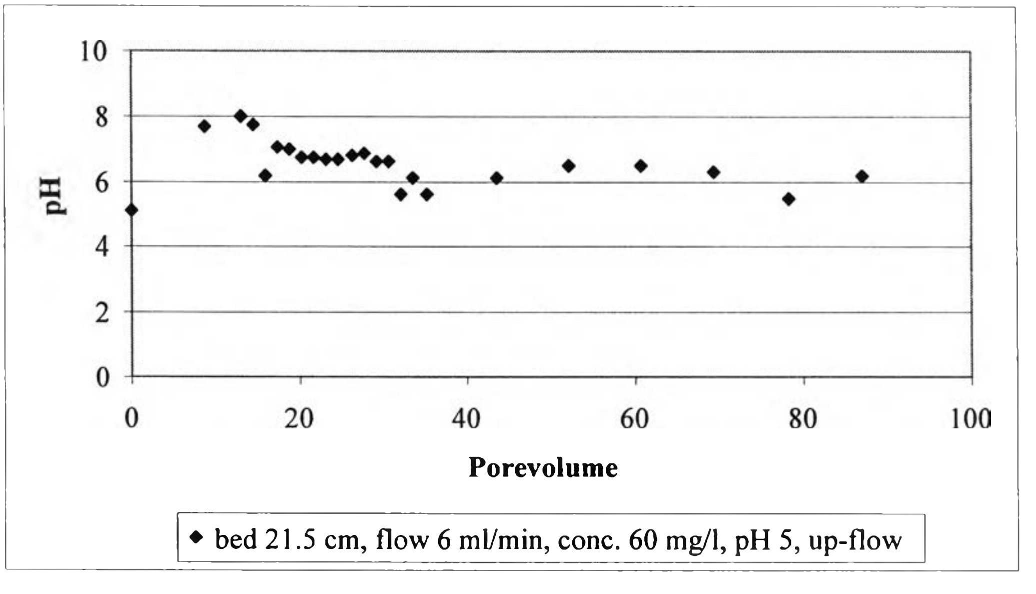

Figure 4.24 pH in the samples under the following conditions: bed 21.5 cm, flow 6 ml/min, conc. 60 mg/l, pH 5, up-flow

With regard to the tendency of the pH value; the first dot at pore volume zero showed the initial pH value of the solution of the influent reservoir, to be near pH 5. Then after the solution was passed through the column system, the value of the pH increased to be higher at pH 7- 8 and then it started declining and became stable at around pH 6.

4.2.6 Blank test

The objective of this part was to investigate the elements present in a sample column of Zn at zero mg/l solution.

Table 4.8 Parameters and their values used to monitor blank test

Parameters	Values
Bed height	21.5 cm
Flow rate	6 ml/min
Initial concentration	0 mg/l
pH	5
Column operation mode	Up-flow

In this experiment, deionize water at pH 5 was fed into the column without zinc. And the samples were collected to analyze for elements. From Figure 4.25 and 4.26 showed that there was Ca released in the effluent solution in the range of 7-10 mg/l. In the mean time, pH of the solution was change after pass through the column from 5 to around 7. It can be seen that Ca released was more systematically related to the amount of Zn fed into the system.

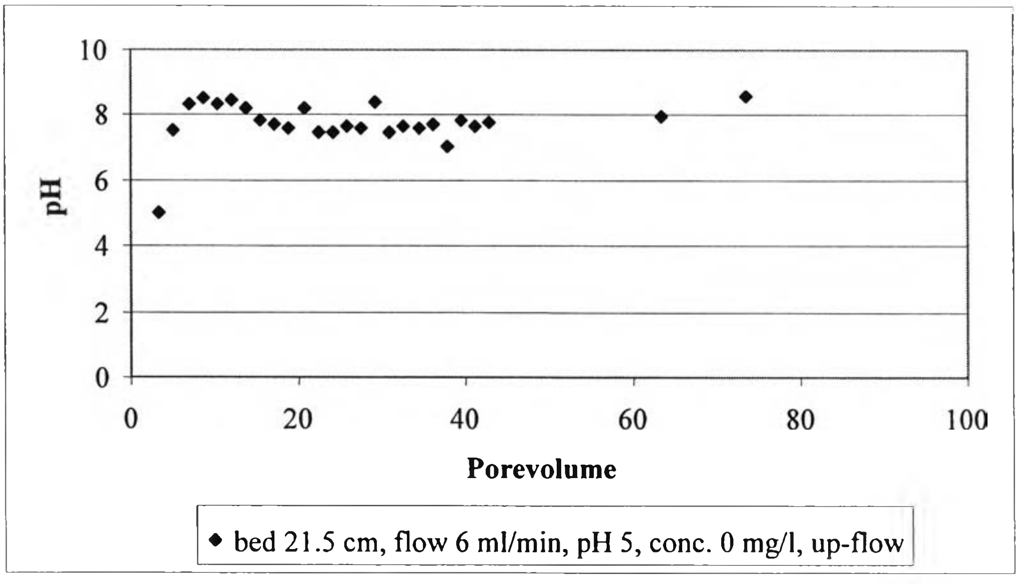

Figure 4.25 pH in the samples under the following conditions: bed 21.5 cm, flow 6 ml/min, conc. 0 mg/l, pH 5, up-flow

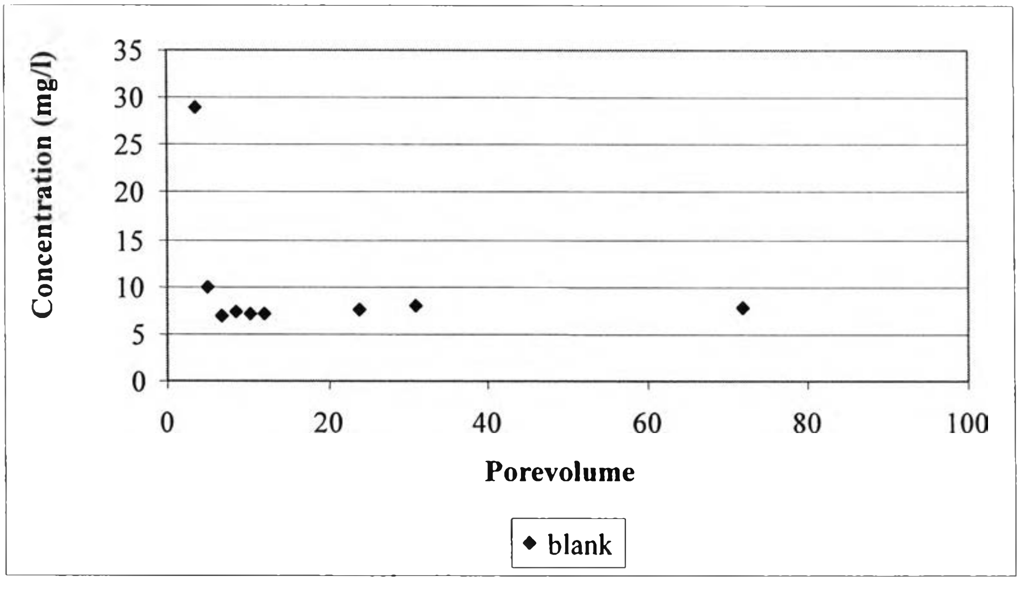

Figure 4.26 Elements concentration in the samples under the following conditions: bed 21.5 cm, flow 6 ml/min, conc. 0 mg/l, pH 5, up-flow

4.3 Foundry sand analysis

Two samples of foundry sand from before and after column experiment were analyzed by two SEM's models. The result of the JSM 5410 model (Figure 4.27-4.28) came out as a picture of foundry sand showing the surface of foundry sand after the experiment was smoother than the one before the experiment, where as the result from JSM 6400 (Figure 4.29-2.30) came out as a graph of count per second (cps) versus kilo electron volt (KeV) as follow:

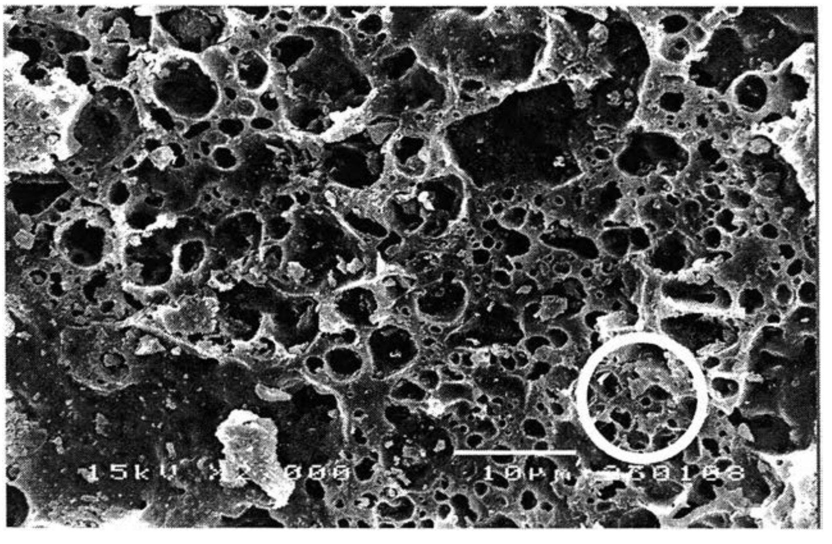

Figure 4.27 Foundry sand surfaces before column experiment

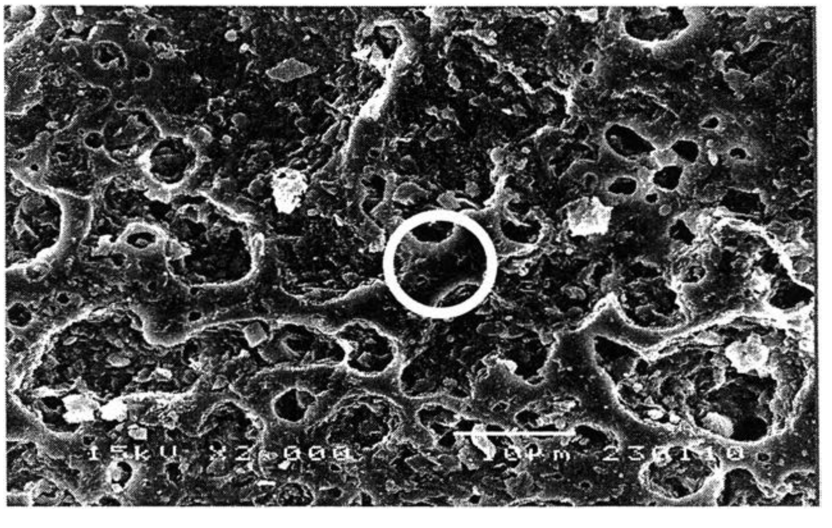

Figure 4.28 Foundry sand surfaces after column experiment

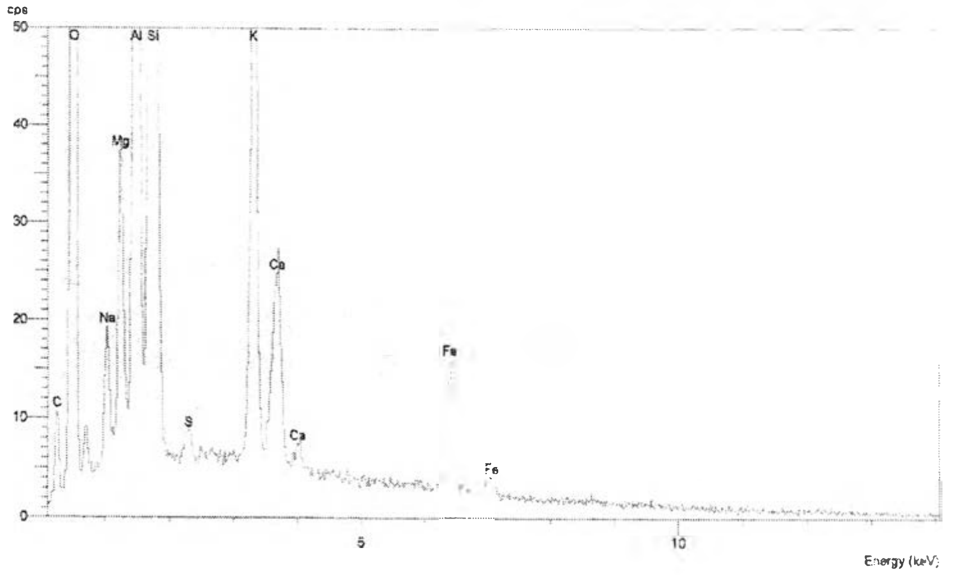

Figure 4.29 Elements in foundry sand before column experiment

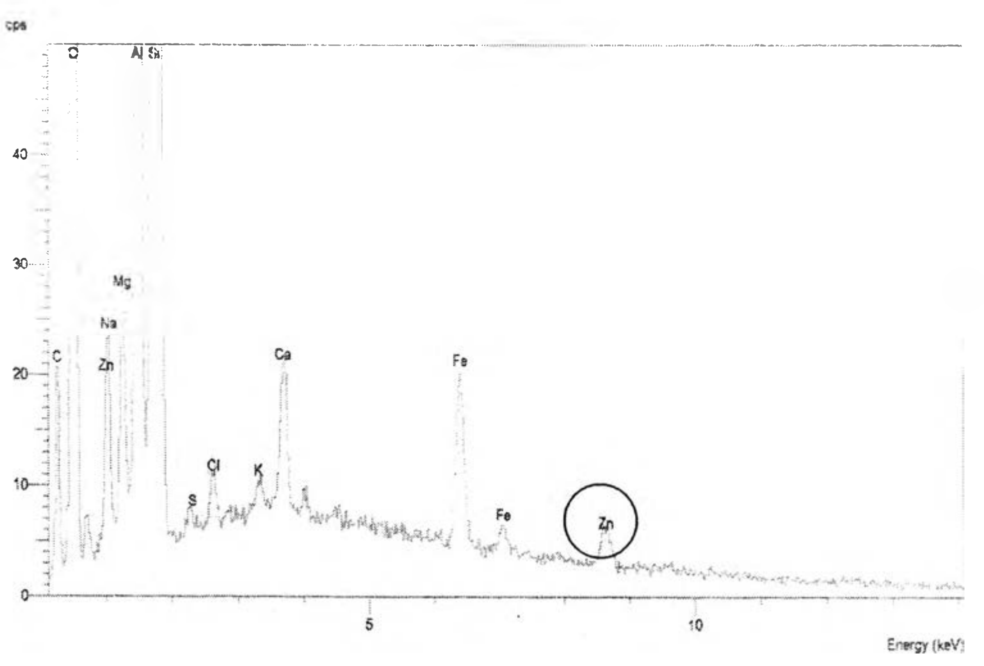

Figure 4.30 Elements in foundry sand after column experiment

Figure 4.27 showed foundry sand surface by using SEM. It can be seen that the surface of foundry sand before experiment was not smooth; there were a lot of pore spaces which resulted in higher surface area of foundry sand.

For Figure 4.28 showed the foundry sand surface at the same magnify level *2000 as the first one for different sand. It can be seen that the surface of foundry sand after the experiment was conduct appeared to be smoother than the previous one.

Figure 4.29-4.30, showed the result obtained by using SEM. The results showed that zinc was found in sand after the experiment, but not in the sand before the experiment. Figure 4.29-4.30, it can be seen that the differences in these two graphs was the amount of substances in foundry sand (K, C, and Zn). The amount of these substances was higher in fresh foundry sand before the experiment than after the experiment. There is some zinc in foundry sand after experiment but not before the experiment. It can however be implied that some form of Zn was present in the sample.

Table 4.9 Compositions of foundry sand before and after column experiment by using XRF

Substances	Concentration wt%
MgO	0.089
Al_2O_3	1.96
SiO_2	89.51
K_2O	2.72
CaO	1.36
TiO_2	0.2
MnO	0.04
Fe_2O_3	2.4
Cu_2O	0.0
ZnO	0.0
Rb_2O	0.02
SrO	0.02
ZrO_2	0.09

(a) before column experiment

Substances	Concentration wt %
MgO	0.10
Al_2O_3	2.05
SiO_2	91.36
K_2O	2.52
CaO	1.15
TiO_2	0.19
MnO	0.04
Fe_2O_3	2.30
Cu_2O	0.01
ZnO	0.15
Rb_2O	0.20
SrO	0.02
ZrO_2	0.09

(b) after column experiment.

According to the results above (Table 4.9) showed that there was no zinc on foundry sand before an experiment but after the experiment zinc was attached with foundry sand.

4.4 Data analysis

The results of the column experiment for each condition was compared to evaluate the performance of each condition and the parameters tested. The raw data obtained from the study was thereafter applied in a real application.

4.3.1 Effect of bed height

Table 4.10 Parameters and their values used to monitor the effect of bed height

Parameters	Values
Bed height	14.5, 18, 21.5 and 25 cm
Flow rate	6 ml/min
Initial concentration	60 mg/l
pH	5
Column operation mode	Up-flow

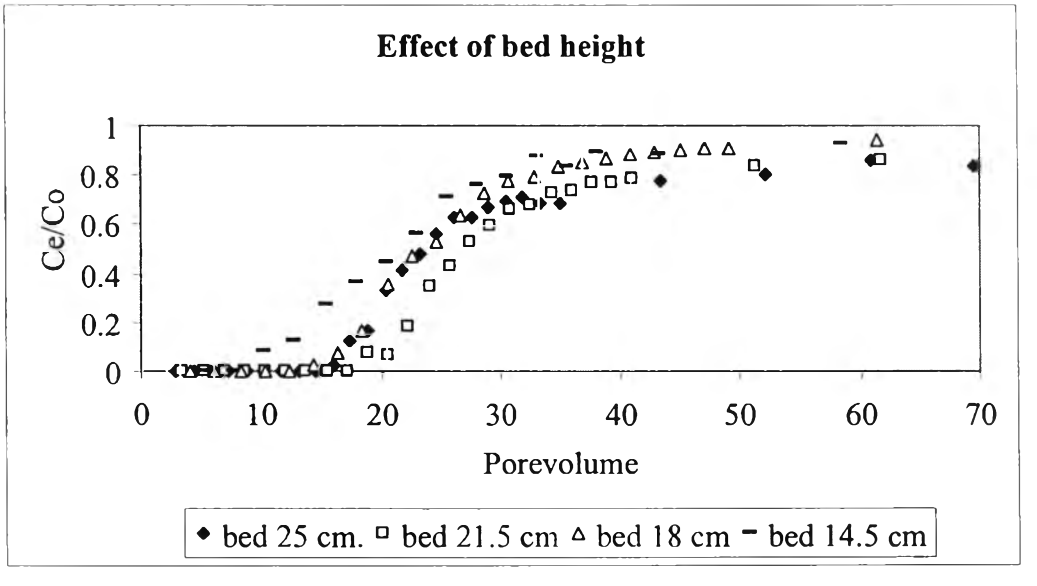

Figure 4.31 Comparison of Zn breakthrough curves at different bed height

The comparison of zinc breakthrough curve at different bed heights (Figure 4.31) showed that at flow rate 6 ml/min, initial concentration 60 mg/l, initial pH 5, up-flow mode, the different of bed height did not affect to breakthrough curves. This might be because of the residence time of the solution in column was more than the reaction time of the removal mechanism took. This may imply that the breakthrough curve of the longer bed height, more than 25 cm, might not effect. The breakthrough curve is expected to be the same as the experiment. The percent of zinc removal increases as the height of the foundry sand column increases. A bed height of 14.5 cm, took the shortest amount of time to reach the breakthrough point. This was followed by a bed height of 18, 21.5 and 25 cm respectively. It can be implied that the reason for the differences in the breakthrough times was due to amount of mass in column. The results thus indicated that shorter bed height had shorter breakthrough time.

With regards to the removal capacity of sand in each of the conditions, the foundry sand of bed 14.5 and 18 cm was not used to its full capacity when compared with the longer ones. This can imply that a short circuit might occur in the column of bed height 14.5 and 18 cm, suggesting that some of the foundry sand in the column of these beds was not used as a result of it not coming in contact with the solution. The removal capacity of the column was therefore, lower than its full capacity.

From the results of the four conditions tested, the total zinc sorbed (mg), percent removal, and the removal capacity of foundry sand (mg/g) was calculated (Table 4.11).

Table 4.11 Result of effect of bed height experiment

Bed height (cm)	percent removal	Zn removal capacity (mg/g)	Residence time (min)	Volume of wastewater treated before breakthrough (ml)	Breakthrough Porevolume
14.5	16.92	0.48	3.9	240	10.16
18	24.14	0.50	4.9	540	18.42
21.5	36.39	0.66	5.8	720	20.56
25	39.35	0.61	6.9	720	17.39

The results of effect of bed height experiment (Table 4.11) indicated that all of bed height had about the same removal capacity, especially bed height of 21.5 and 25 cm. While, the percent removal increases with the increasing of the bed height, the performance of the foundry sand column was attributed to the removal of zinc in shallower columns. Smaller amounts of sand results in a decreased availability of the removal site of zinc; therefore there was a smaller percentage of zinc removed in the foundry sand column. The passage of a smaller volume of the effluent sample would cause the adsorption sites to fill up and exhaust the removal capacity of the foundry sand. At the same time, the zinc removal capacity of foundry sand and the amounts of Ca^{+2} released at each bed height (14.5, 18, 21.5, and 25 cm) were 0.48, 0.5, 0.66, and 0.61 mg/g, respectively, and 0.44, 0.5, 0.46, and 0.46 mg/g, respectively.

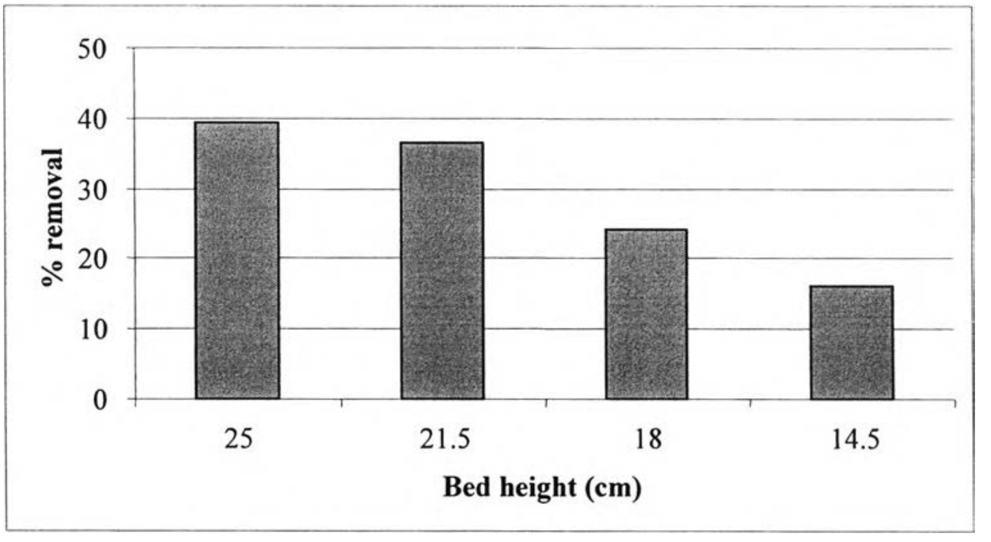

Figure 4.32 Relationship between the changed of bed height and percent removal from effect of bed height experiment

In regards to the relationship between the bed height and percent of zinc removal (Figure 4.32), the results indicated that a higher bed height results in a higher percent removal. The higher bed height consists of higher medium mass, which result in the higher surface area. The greater the surface area available, the higher the sorption of zinc sorbed onto the foundry sand. Predicting the amount of zinc removal can be done by using the data of the Zn removal capacity of foundry sand.

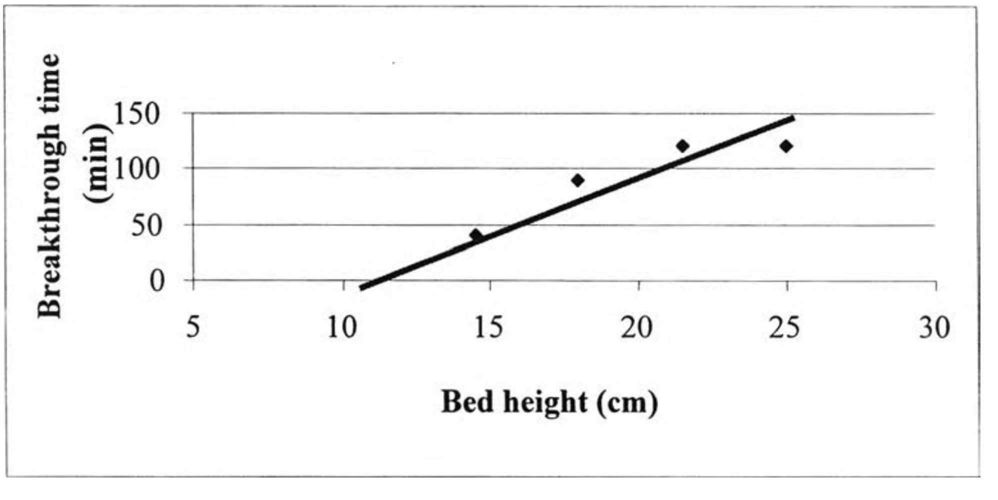

Figure 4.33 Relationship between breakthrough time and bed height

Figure 4.33 showed the relationship between breakthrough time and bed height. The graph indicated that the breakthrough time increased with an increased in bed height. This result suggested that the more foundry sand present in the column, the longer the time the wastewater can be treated. The trend line indicated that the critical bed height was around 11 cm long. This length may also represent the length of mass transfer zone of foundry sand. The shorter bed height would have breakthrough at the beginning.

4.3.2 Effect of flow rate

Table 4.12 Parameters and their values used to monitor the effect of flow rate

Parameters	Values
Bed height	25 cm
Flow rate	6, 11, and 15 ml/min
Initial concentration	60 mg/l
pH	5
Column operation mode	Up-flow

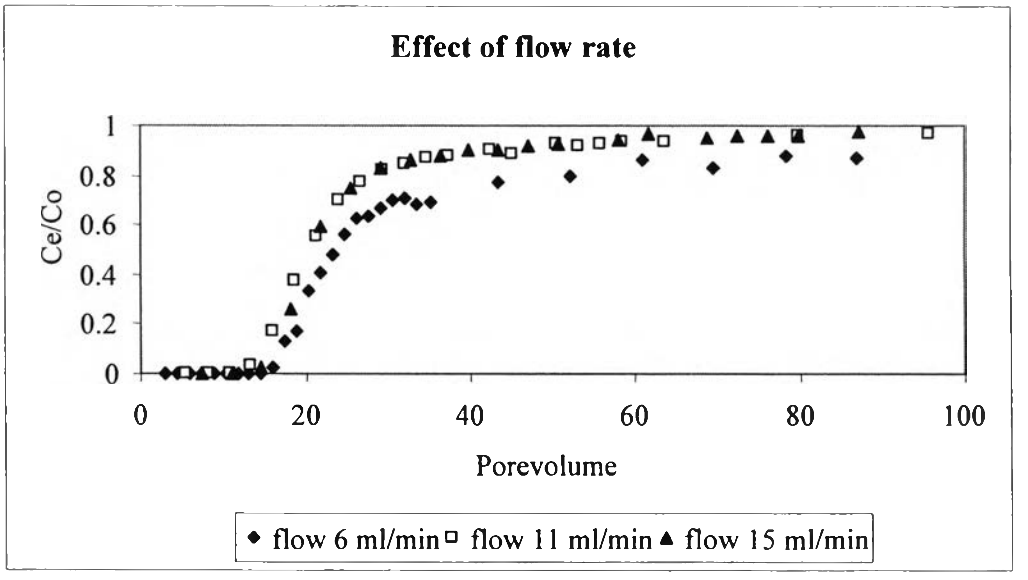

Figure 4.34 Comparison of zinc breakthrough curve at different flow rates

The comparison of zinc breakthrough curve at different flow rates (Figure 4.34) showed that a flow rate of 6 ml/min took the longest time (17.39 pore volume) to reach its breakthrough point, followed by flows 11 ml/min and 15 ml/min (15.94 and 14.5 porevolume, respectively). The reason for the difference in the breakthrough times was the contact time between the wastewater and foundry sand (RPI, 1996; Vijayaragravan, 2005). Among all the flow rates, at flow rate 6 ml/min aqueous solution was fed into the column the slowest; hence, its contact time was the highest. The time that the solution of wastewater had contacted with the foundry sand in the column was longer at a flow rate of 6 ml/min than at flows rates of 11 ml and 15 ml/min. The mechanisms occurring in the column at this flow rate was believed to be more completed than the others which can be observed by the percent of zinc removal. Thus, the most completed mechanism which occurred in the column resulted in it having the highest percent removal.

From the results of the three conditions above, total zinc sorbed (mg), percent removal, and the removal capacity of sand (mg/g) was calculated and are shown in Table 4.13.

Table 4.13 Total zinc sorbed (mg), percent removal, and the removal capacity of sand (mg/g) calculated from results of effect of flow rate experiment.

Flow rates	Residence time (min)	percent removal	Breakthrough Porevolume	Zinc removal capacity (mg/g)
6	6.9	39.35	17.39	0.61
11	3.8	16.85	15.94	0.45
15	2.8	13.01	14.5	0.48

From Table 4.13 and Figure 4.35, it can be observed that an increase in flow rate resulted in a decrease of percent removal. It can be inferred that between fast flow (11 and 15 ml/min) and slow flow (6 ml/min), slow flow had better zinc removal efficiency. When comparing the results of breakthrough time and flow rate it showed that slow flow had the longest time and the highest zinc removal capacity.

The data of the percentage of zinc removed was plotted against the value of the flow rate to find the relationship between these two parameters. The results revealed that a higher flow rate resulted in a lower percent removal. The percent removal and flow rate was thus related.

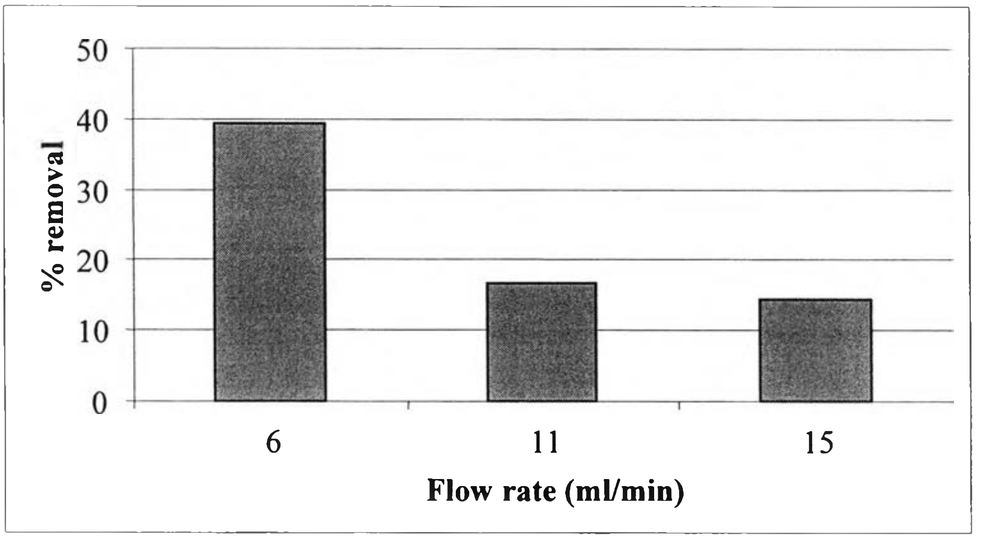

Figure 4.35 Relationship between flow rate and percent removal from effect of flow rate experiment

4.3.3 Effect of initial concentration

Table 4.14 Parameters and their values used to monitor the effect of initial concentration

Parameters	Values
Bed height	21.5 cm
Flow rate	6 ml/min
Initial concentration	30, 60 mg/l
pH	5
Column operation mode	Up-flow

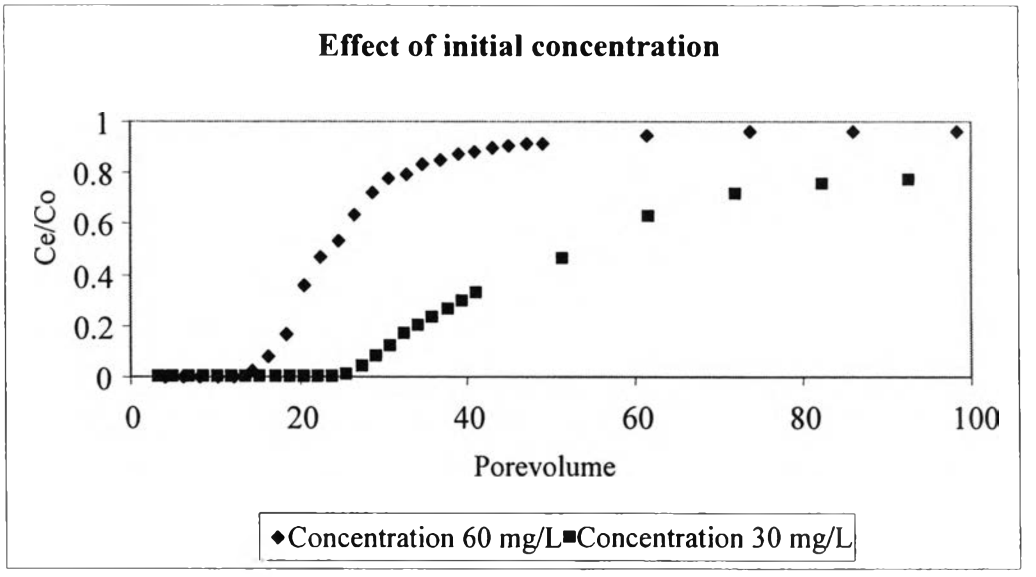

Figure 4.36 Comparison of zinc breakthrough curve at different initial concentrations

The comparison of zinc breakthrough curve at different initial concentrations (Figure 4.36) showed that an initial concentration of 30 mg/l had a longer breakthrough as was expected. This was due to the fact that a higher concentration will occupy the surface area of the foundry sand faster. As a result of similar capacity of sand, the amount of zinc that can be sorbed by foundry sand is equal. Thus an initial concentration of 60 mg/l will provide a higher amount of Zn when compared to 30 mg/l at the same period of time. The foundry sand will therefore reach its full capacity faster than the initial concentration of 30 mg/l that provides smaller amounts of zinc at a time. Moreover, the removal capacity of both conditions described in Table 4.15 indicated that the initial concentration might not significantly affect the removal capacity of foundry sand. Only the breakthrough and exhaustion times were affected. This implies that different concentrations affect only the exhaustion time which was caused by the speed of zinc fed into the column.

Table 4.15 Results of effect of initial concentration experiment

Initial Concentration (mg/l)	Zn removal capacity (mg/g)	Breakthrough Porevolume	Exhaustion Porevolume
30	0.58	30.84	102.0
60	0.66	20.56	102.8

4.3.4 Effect of initial pH

Table 4.16 Parameters and their values used to monitor the effect of initial pH

Parameters	Values
Bed height	21.5 cm
Flow rate	6 ml/min
Initial concentration	60 mg/l
pH	3 and 5
Column operation mode	Up-flow

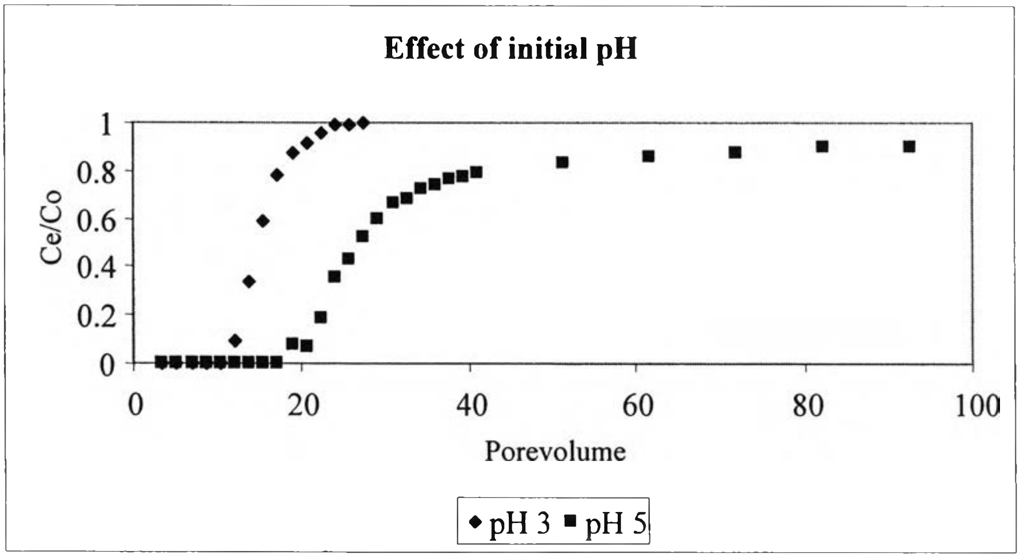

Figure 4.37 Comparison of zinc breakthrough curve at different initial pH

The effect of pH on the removal of zinc (Figure 4.37) was observed in the increasing trend at pH 3 in comparison to the trend at pH 5. The removal was 0.29 mg/g or 35.23 mg at pH value 3 and 0.66 mg/g or 78.87 mg at pH 5. These results were in contrast with the findings of Zeng (2002), which showed that the pH did not have a major effect on the removal of Cu^{+2} from solution by algal biosorbent. However, Jose (1998) noted that the metal uptake increased as the pH was increased (from pH 3 to 5). It was concluded that the variation in the removal efficiency due to the solution pH was attributed to the exchange of zinc ions at a higher pH. As the pH increased, there was an increasing trend in the concentration of anion on the foundry sand surface from PZC 2.9 which led to the greater attachment of zinc ions from the solution. However, there were some researches stated that low pH or acidic conditions usually create competition between protons (H^+) and heavy metals (M^{2+}) at the binding site of mediums (Volesky, 1990; Sungkhum, 2003 and Apiratikul et al., 2004).

At high pH values, the metal speciation in solution became an important factor in metal uptake. The reduction in metal uptake, as the pH was increased beyond its optimum values (pH 5 to 7), had been attributed to reduced solubility and the precipitation of metals (Josed, 1998).

Table 4.17 Results of effect of initial pH experiment

Initial pH	**Zn removal capacity (mg/g)**	**Ca Released (mg/g)**	**Breakthrough Porevolume**
3	0.29	0.50	11.00
5	0.66	0.46	20.56

Table 4.17 indicated that the zinc removal capacity (0.29 mg/g) and breakthrough porevolume of an initial pH of 3 were less than those of an initial pH of 5. This showed that foundry sand had higher removal efficiency at pH 5 solution than pH 3.

4.3.5 Effect of column operation modes

Table 4.18 Parameters and their values used to monitor the effect of column operation modes

Parameters	Values
Bed height	21.5 cm
Flow rate	6 ml/min
Initial concentration	60 mg/l
pH	5
Column operation mode	Up-flow and down-flow

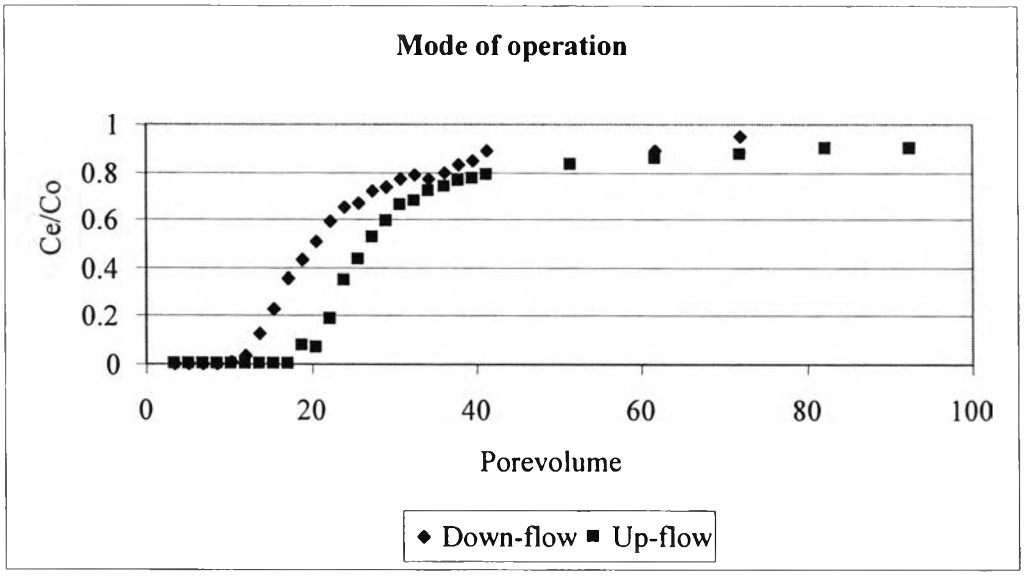

Figure 4.38 Comparison of zinc breakthrough curve at different column operation modes

It can be observed in Figure 4.38, that the curves of the up-flow and down-flow mode of operations were different especially with regards to breakthrough time. In addition, the data in table 4.19 suggest that the percentage of zinc removal and zinc removal capacity of these two conditions were different at this flow rate. The breakthrough time of down-flow was earlier than up-flow mode and the breakthrough time of up-flow was almost twice that of down-flow mode. Thus, the amount of zinc removed before breakthrough should be considered. Table 4.19 also showed that the amount of zinc removed before breakthrough by down-flow was only 61.2 percent of up-flow mode. This suggests that a short circuit might occur in down-flow mode and hence, the selection of column operation mode between up-flow and down-flow should be considered based on the cost of each kind of operation. Up-flow mode might have a higher cost of electricity while down-flow mode might have a higher cost of medium, transportation and labor because it had to change medium more often. In such cases, the lower cost is recommended for removal process.

Table 4.19 Results of mode of operation experiment

Mode of operation	**percent removal**	**Zn removal capacity (mg/g)**	**Volume of wastewater treated before breakthrough (ml)**	**Breakthrough Porevolume**
Up-flow	36.39	0.66	720	20.56
Down-flow	26.96	0.51	378	12.00

4.3.6 The mechanisms in column

In order to find the mechanisms that occurred in column experiment, the following three methods were performed to prove that each mechanism had the potential to occur. First the data from the column experiment was analyzed to find the relationship of the amount of substance in the samples that could indicate what mechanism might be occurring based on the theoretical knowledge explained in Chapter 2.

The results indicated that the amounts of Zn^{+2} and Ca^{+2} in the sample changed inversely. This suggests that ion exchange had potentially occurred in the column along with other sorption mechanism. As it can be seen from results of the blank, feeding of Zn was somehow related to the amount of Ca released in a systematic way. Table 4.20 indicated that the ratio of Zn:Ca was almost proportional ranging from 1:1 to 1:2.

Table 4.20 Amount of zinc sorbed on foundry sand and calcium released into solution

Conditions	Zinc (mmole/g)	Calcium (mmole/g)
Bed 14.5 cm. flow 6 ml/min	0.007	0.010
Bed 18 cm. flow 6 ml/min	0.008	0.010
Bed 21.5 cm. flow 6 ml/min	0.010	0.010
Bed 25 cm. flow 6 ml/min	0.010	0.010
Bed 25 cm flow 11 ml/min	0.007	0.013

The theoretical knowledge of the ion exchange mechanism, states that the in-out exchange of ions has to be balanced or equal. This is in contrast to the data obtained in this experiment, which indicated that the amount of Zn^{+2} sorbed was more than that of Ca^{+2}. When considering the net negative charge above PZC, the higher the pH of the solution, the more the negative charges available on the surface which zinc can adsorb on. It can therefore, be concluded that adsorption might occur along with the ion exchange.

The physical properties of foundry sand shown in Table 4.21 showed that foundry sand from Siam Nava Industry Co., Ltd. had 20.84 % clay content. Since this clay was Calcium-Bentonite, it allowed for the exchange of Ca^{+2} with Zn^{+2}. This was similar to the results of Lee and Benson, (2002).

Table 4.21 Physical properties of the spent foundry sands

Sample	**Clay content (%)**	**Total Iron Content (%)**	**Percent TOC**
Siam Magotaux Co., Ltd.	19.14	4.37	2.03
Siam Nava Industry Co., Ltd.	10.84	0.48	1.82
Siam Navaloha Foundry Co., Ltd.	1.44	4.46	1.17
Asian Autopart Co., Ltd.	0.00	0.00	0.47

Available from: Thunsiri (2004)

The change in pH that occurred in the sample in different times can be attributed to buffering reactions. For the foundry sands, buffering was probably caused by the carbonate minerals, exchangeable base cations, and decomposition of aluminosilicate minerals (Lee, T. and Benson, C., 2002). For the Peerless iron, the pH change can be attributed primarily to corrosion of the iron (Lee and Benson, 2002).

4.5 Environmental management

From the experimental results indicated that foundry sand has ability to remove zinc from contaminated water. As the best condition of bed height 25 cm, flow rate 6 ml/min, initial pH 5, initial concentration 60 mg/l, up-flow mode, the foundry sand from Siam Nava industry has a capacity of 0.66 mg/g. This foundry sand can be applied as a low cost sorption media to remove zinc, a toxic substance from the production process within factory, at the tertiary part of wastewater treatment process.