CHAPTER III

METHODOLOGY

The study was conducted in three phases. In phase 1, one type of foundry sand was chosen from among four types to conduct the experiments in phase 2 and 3. In phase 2, the column experiment was conducted. The metal concentration in the samples was monitored at different periods in the experiment until the column was exhausted. And finally, in phase 3, the result was calculated to determine the performance of the column under different conditions.

3.1 Material and apparatus

3.1.1 Equipments

- pH meter, HACH Sension 3
- Digital Balance (4 digits), Sartorius, BP2215
- Water Purification System (For making DI water), ELGA, Ultra analytic
- Inductively Couple Plasma spectrometer (ICP) , Varian Vista-MPX CCD Simultaneous ICP-OES
- Scanning Electron Microscope (SEM), JEOL, JSM 5410 LV
- SEM, JAO, JSM 6400 link ISIS Series 300
- X-Ray fluorescence spectrometer (XRF)
- X-Ray Diffraction spectrometer(XRD)

3.1.2 Glass wares

- Volumetric flasks
- Glass watches Beakers
- Pipettes
- Cylinders
- Droppers
- Teflon bottles

3.1.3 Chemical Reagents

- Analytical grade $ZnCl_2$
- HNO_3 Concentration at 69%
- NaOH anhydrous
- Deionized water (DI water)
- pH buffer solution 4.00 $\pm$ 0.02, HACH
- pH buffer solution 7.00 $\pm$ 0.02, HACH
- Mix metal standard solution for ICP, MERCK
- Analytical grade NaN_3

3.1.4 Foundry sands

- Siam Magotaux Co., Ltd
- Siam Nava Industry Co., Ltd.
- Siam Navaloha Foundry Co., Ltd.
- Asian Autopart Co., Ltd.

3.2 Foundry sand selection

Four types of foundry sand were obtained from different factories in Saraburi Province, Thailand: Siam Magotaux Co., Ltd., Siam Nava Industry Co., Ltd., Siam Navaloha Foundry Co., Ltd., and Asian Autopart Co., Ltd. respectively. Based on the results of batch experiments carried out by (Thunsiri, 2004), one type was chosen to conduct the experiment in phase 2. The percent removal of each foundry sands from batch experiment is shown in Table 3.1.

Table 3.1 Percent removal of foundry sand from the batch experiment

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)

The criteria for selecting the foundry sand for phase 2 were:

1. The foundry sand shows the highest zinc removal ability.
2. The foundry sand is not considered a hazardous waste nor does it leach or contain hazardous substances. This will be determined in the leachability test.
3. The foundry sand should have high permeability. In other words, aqueous solution must be able to pass through well, since this sand is aimed to be used as a medium for treating large volumes of wastewater in a short time. (This criteria was tested in the preliminary investigations)

Table 3.2 Leachability of heavy metals from 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)

3.3 Column experiment

The foundry sand chosen in foundry sand selection part was used as a medium in the column experiment. The synthetic wastewater in the influent reservoir was pumped through the column from the bottom up to the top of column for the "up-flow mode" and from the top down to the bottom of the column for the "down-flow mode" using peristaltic pumps at different flow rates. The outlet end of the column was connected to the delivery line that ends at the effluent reservoir (Figure 3.1).

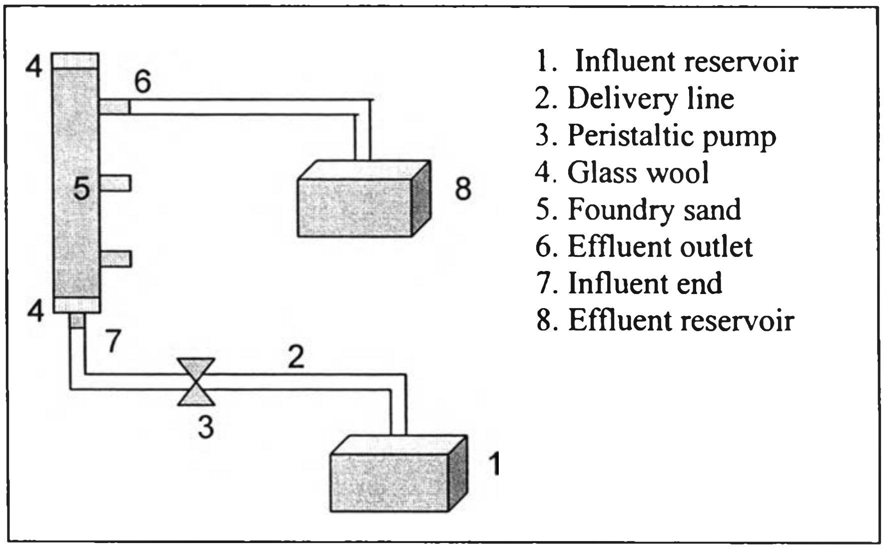

Figure 3.1 Column experimental setup

3.3.1 Glassware preparation

All glassware was immersed glassware in 20% HNO_3 overnight. The following day, they were soaked in water for a few hours, then rinse with deionized water. All glassware was dried in an oven before use.

3.3.2 Preparation for synthetic wastewater

Synthetic wastewater was prepared by dissolving zinc chloride in deionized (DI) water to yield the expected zinc concentration to be used under different conditions. Sodium azide (0.1% by weight) was added to the mixture to prevent biological activity and the pH was adjusted with 0.1 M nitric acid or 1.0 M sodium hydroxide to yield the expected initial pH.

Fixed-bed column experiments were conducted using acrylic columns (internal diameter 25 mm, length 400 mm) packed with foundry sand. Glass wool was inserted at both ends of the column in order to support and prevent the medium from floating or leaking.

A peristaltic pump was used to charge the Zn-bearing water through the foundry sand packed column at desired flow rates.

The samples were collected at the effluent reservoir at different time intervals and were analyzed for metal concentration and pH. In accordance with the standard method (inductively coupled plasma method 3120), the sample was preserved at pH<2 by using HNO_3. The total zinc was analyzed using a Varian Vista-MPX CCD Simultaneous ICP-OES. A pH meter (HACH Sension 3) was used to measure the pH. In this study, all experiment was carried out in duplicates, and triplicate samples were analyzed.

The column studies were aimed at evaluating the effects of various operational parameters, such as the initial zinc concentration, the medium's mass (the bed depth), and the flow rate.

Time zero of the experiment was designated as the point when the solution reached the bottom of the column that was packed with fresh foundry sand with no pretreatment process.

The following parameters were studied in the experiment:

1. Bed height
2. Flow rate
3. Initial concentration
4. Initial pH
5. Mode of column operation

3.3.3 Effective of parameters

3.3.3.1 Effects of bed height

This experiment was done to observe the critical bed height, which is the shortest bed height that can treat contaminated water effectively. The various bed heights were considered based on literature reviews (Vijayaraghavan et al. (2004); Vijayaraghavan et al. (2005); etc.) that used 30 cm column heights. In this study, however, the column can vary the highest bed height to be at 25 cm. due to the final outlet height of 27 cm and the lowest bed height to be at 14.5 cm This was determined in the preliminary investigation which showed that a bed height shorter than 14.5 cm could cause the breakthrough at the beginning meaning that the column cannot reduce the Zn to go below the effluent standard (5 mg/l) at the flow rate of 6 ml/min. The 14.5 cm of bed height therefore investigated as the minimum bed height.

In the experiment to monitor the effects of bed height, a known quantity of foundry sand was placed in the column to yield the desired bed heights. 80, 100, 120, and 140g of foundry sand were placed in the column to yield bed height of 14.5, 18, 21.5, and 25 cm, respectively, or the equivalent medium volume of 76.95, 95.52, 114.09 and 134.88 cm^3, respectively at bed density of around 1.05 g/cm^3.

3.3.3.2 Effects of flow rate

This experiment was done to investigate the effect of flow rate and to find the flow rate that yielded the maximum removal efficiency, i.e., allowing enough contact time. Three flow rates were considered as was done in previous studies. (Vijayaraghavan et al. (2004); Vijayaraghavan et al. (2005); Apiratikul. (2004); etc.)

The following factor was considered is the stabilization of the media. The flow rates did not fluidize the media bed in the column. This is important since higher flow rates can affect the density and pore volume of the medium in the column as can be observed by monitoring the movement of sand particle in the column. The bed height used in this experiment was at 25 cm which was the highest height to avoid the effect of bed height as much as possible.

Table 3.3 Variables and values for the bed height experiment

Variables	**Values**
Independent variables	
1. Bed heights	14.5, 18, 21.5, and 25 cm
2. Duration of sample collection	Every 10 min for the first 4 hrs. After that every 1 hr for 7 hrs or until column is exhausted.
Fixed variables	
1. Initial concentration of zinc	60 mg/l
2. Initial pH	5
3. Flow rates	6 ml /min
4. Column operation	Up-flow
Dependent variables	
Effluent characteristic	- Concentration of elements in sample - pH

Table 3.4 Variables and values for the flow rate experiment

Variables	**Values**
Independent variables	
1. Flow rates	6, 11 and 15 ml/min
2. Duration of sample collection	Every 10 min for the first 4 hrs. After that every 1 hr for 7 hrs
Fixed variables	
1. Initial concentration of zinc	60 mg/l
2. Initial pH	5
3. Bed height	25 cm
4. Column operation	Up-flow
Dependent variables	
Effluent characteristic	- Concentration of elements in sample - pH

3.3.3.3 Effects of initial concentration

This experiment was done to investigate the effects of initial concentration on parameters; such as the breakthrough time, and the removal capacity, since the different zinc concentrations in wastewater from different factories can affect the removal efficiency, especially in the way of increase or decrease in Zn mass.

Table 3.5 Variables and values for the initial concentration experiment

Variables	Values
Independent variables	
1. Initial concentrations of zinc	30 and 60 mg/l
2. Duration of sample collection	Every 10 min for the first 4 hrs. After that every 1 hr for 7 hrs or until column is exhausted.
Fixed variables	
1. Flow rate	6 ml/min
2. Initial pH	5
3. Bed height	21.5 cm
4. Column operation	Up-flow
Dependent variables	
1. Effluent characteristic	- Concentration of elements in sample - pH

3.3.3.4 Effects of initial pH solution

The effect of pH on the removal of zinc was examined because the wastewater from factories has various pH values. Generally it is considered that wastewater from the plating industry is acidic. Therefore, the effect of the pH on the removal of zinc was considered in the pH range of 3-5. The higher pH than 5 will cause precipitation to occur in order to avoid that mechanism from occurring in the column. This can clog pores and affect the efficiency of column. Two pH values were investigated in this study. For a particular flow rate, the effect of pH could then be compared. The outcome result from this part can be used as a recommendation data for a real application.

Table 3.6 Variables and values for the initial pH experiment

Variables	Values
Independent variables	
1. Initial pH	3 and 5
2. Duration of sample collection	Every 10 min for the first 4 hrs. After that every 1 hr for 7 hrs or until column is exhausted.
Fixed variables	
1. Flow rate	6 ml/min
2. Initial concentration	60 mg/l
3. Bed height	21.5 cm
4. Column operation	Up-flow
Dependent variable	
Effluent characteristic	- Concentration of elements in sample - pH

3.3.3.5 Effects of mode of the column operation

There were two modes of column operation, up-flow and down-flow. Up-flow was done by feeding wastewater from the bottom. The water filled the pore space. The medium became saturated and the water level rose up to the top of the column. This behavior suggests that the medium was used to its full capacity or every pore of medium was in contact with the solution.

In contrast, in down-flow column mode, the wastewater was fed from the inlet end at the top of column. When the wastewater moved down through the medium, there is a possibility that it can have short circuit occurring due to the differences in medium packing density and effect of gravity. Wastewater tends to move through the area that have lower density since some parts of the medium is no in contact with solution. In such cases, parts of the column were not used and the column became exhausted faster. Although there was an equal density of medium packed throughout the column, short circuit might or might not occur. This study was therefore, done to find out the effect of mode for column operation. The data will be used for the selection of mode in real application.

Table 3.7 Variables and values for the effect of mode experiment

Variables	**Values**
Independent variables	
1. column operation mode	Down-flow and up-flow
2. Duration of sample collection	Every 10 min for the first 4 hrs. After that every 1 hr for 7 hrs or until column is exhausted.
Fixed variables	
1. Flow rate	6 ml/min
2. Initial pH	5
3. Bed height	21.5 cm
4. Initial concentration	60 mg/l
Dependent variables	
1. Effluent characteristic	-Concentration of elements in sample, pH

3.4 Foundry sand analysis

The objective this part of the study was to find out the differences between foundry sand before and after experiment. The result of this study was to observe the small particle of foundry sand, which indicated the change in physical properties of foundry sand. This will lead to a better understanding of the mechanism that occurred in the experiment.

The equipments in this part are

- Scanning Electron Microscopes (SEM), JEOL, JSM 5410 LV
- SEM, JAO, JSM 6400 link ISIS Series 300

The first equipment was used to observe the real pictures of foundry sand surface both before and after column experiment. This equipment can enlarge the level of photo to see a bigger or smaller piece of foundry sand. Comparison of two photos was analyzed at the same level.

A different model of SEM (JSM 5410 and JSM 6400) was used for qualitative analysis, to analyze the potential amount of elements in foundry sand. Since the previous equipment JSM 5410 could not indicate the pictures, the result from JSM 6400 was used to predict the composition of element in the former picture.

3.5 Data analysis

Metal concentration data from phase 2 will be plotted for breakthrough curve to show the differences among conditions.

The results were plotted for:

(a) pH versus pore volume

$$\text{Pore volume} = \frac{Vwater}{Vo} \quad (3.1)$$

$$Vo = \text{porosity} * V_T \quad (3.2)$$

$$\text{Porosity} = \frac{\text{wet mass - dry mass}}{\text{dry mass}} \times 100 \quad (3.3)$$

Where as;

V_T = volume of medium

V_{water} = volume of water pass through the column

V_o = Pore volume of foundry sand

(b) Zn concentration of sample versus pore volume at

- Various initial concentrations
- Various initial pH
- Various mass of medium
- Various flow rates

(c) Metal concentration versus pore volume at

- Various metal ions

In this case, there is Ca present in the effluent sample. The concentration of Zn and Ca was plotted to find the relationship that occurred.

And the results were calculated to see:

3.5.1 Sorption capacity of sand (q)

Sorption capacity is the capacity of foundry sand packed column that indicates the approximate amount in milligram of zinc sorbed by one gram of foundry sand. This value can use to find to amount of sand to sorbed zinc in wastewater. And it can use to compare the capacity of zinc sorbed with other mediums.

$$\text{Sorption capacity (q)} = Zn_{sorbed} / Mass_{medium} \ (mg/g) \quad (3.4)$$

3.5.2 Percent Removal

This is used to calculate the percent of zinc sorbed by foundry sand packed column compared with the total amount of zinc fed in the column. This value is used to compare the efficiency of each condition at the same porevolume.

$$\% \text{ removal} = (Zn \text{ sorbed} / Zn \text{ in}) * 100 \quad (3.5)$$

3.5.3 Breakthrough time (hr)

This is used to compare the time of column under operation to remove zinc until the effluent concentration exceeds the standard.