CHAPTER III
METHODOLOGY

This research studied the feasibility of using saline groundwater to treat the chromium contaminated wastewater. The scope of this research is as follows.

1) Study of characteristics of saline groundwater collected from different locations to the nearest available salt mills in Khon Kaen, Udon Thani, Mahasarakam and Nakonratchasima Province. Then pH, Mg, Ca, Na, Cl, acidity and alkalinity of saline groundwater samples were analyzed.
2) Preparation of white slurry of groundwater with alkaline reagent. Calcium and magnesium contained in saline groundwater can be precipitated as metal hydroxide and carbonate under the optimum pH.
3) Precipitation of chromium contaminated in the tanning wastewater with the alkalinized ground water under controlled pH level. Chromium was in the precipitated form of $Cr(OH)_3$.
4) Recovery of chromium by acidification with H_2SO_4 under control pH. The precipitate chromium hydroxide can be dissolved as $Cr_2(SO_4)_3$, which can then be reused for the tanning process.
5) Implementing the laboratory scale finding to the model scale test.

The experiments were performed as described below.

3.1 Material

3.1.1 Samples

After pre-investigation of saline groundwater characteristics from those mentioned three provinces, it was decided to select saline groundwater at Bandung District, Udon-Thani Province for this study. Saline groundwater samples were collected twice a month for the period of 4 months covering dry and rainy seasons to compare the mineral content in different seasons.

Tanning wastewater was collected from the tannery factory, Khon Kaen Tanner Group Co. Ltd., in Phon District, Khon Kaen Province.

3.1.2 Chemicals

All reagents were of analytical grade including sodium hydroxide, nitric acid, sulfuric acid.

Ultra pure water with conductivity less than 0.1 μS was obtained from a Milli-Q system (Millipore, Bedford, MA, USA)

Standard solution of metals was prepared by serial dilution of stock standard solutions of each metal containing 1000 mg/L.

All standards and samples were stored in the clean polyethylene bottles as the recommended procedures for trace metal determination.

3.1.3 Instruments

Chromium deytermination was made by Atomic absorption spectrophotometer (AAS 6401F, Shimadzu, Japan)

Chromatographic analyses were performed on a metal-free high- pressure ion chromatography, DX-100 (Dionex, Sunnyvale, CA, USA). A Rheodyne injector with sample loop 25 μL was required.

The Dionex IonPac CS12 analytical column (250 mm x 4 mm I.D., 9 μm bead diameter, ethylvinyl benzene-functionalized with sulfonate functional group) was used for cations separation. The 50 mm x 4 mm I.D. IonPac CG12 guard column was placed prior to the IonPac CS12 to prevent potential fouling of the analytical column. All measurements were made isocritically at room temperature and all samples were filtered through a 0.45 μm filter prior to injection.

All pH measurements were performed by pH meter (USA.).

3.2 Methodology

3.2.1. Analysis of Saline Groundwater.

Saline groundwater wells were selected from the nearby salt mills in Khon Kaen, Udon Thani, Mahasarakam, and Nakonratchasima Provinces. Analysis of groundwater characteristics was then analyzed. Then, the well that shows the highest concentration of magnesium and calcium. was selected to use for the experinments. Of the four sites, Bandung District of Udon-thani Province shows the highest

magnesium (Mg) and calcium (Ca) concentration. Then, the groundwater samples were taken from Bandung District, Udon-thani Province. Samples were analyzed for pH, magnesium (Mg), calcium (Ca), sodium (Na), chloride (Cl). Groundwater samples were taken twice a month for 4 months covering dry and rainy season in order to compare the mineral content in such seasons.

3.2.2 Preparation of white slurry by alkalinization with Sodium hydroxide

Preparation of the white slurry was made by adding sodium hydroxide (NaOH) to the groundwater sample to precipitate metal hydroxide and carbonate as magnesium hydroxide, $Mg(OH)_2$,. and calcium carbonate, $CaCO_3$. From literature review, it was found that the best pH for the precipitation of $CaCO_3$ and $Mg(OH)_2$ are approximately 12.5 (Ayoub, 1999). The sample of saline groundwater which was collected from different locations and time contained various concentration of calcium, magnesium and other minerals. Therefore, the optimum pH level of the sample would have to be determined by varying the pH level in the ranges of 12-13.5. As this research was only interested in the concentration of calcium and magnesium, other minerals would be disregarded. The optimum pH level were determined as follows.

- Filling four beakers with 500 ml saline groundwater.
- Adding NaOH solution to raise pH of the samples to 12-13.5
- Mixing the solution for 3-5 minutes.
- Allowing the precipitate to settle for 6 hours.
- Draining the supernatant out and collect the precipitate (white slurry).
- Analyzing the Ca and Mg content of the white slurry

3.2.3 Precipitation of Chromium Tanning Wastewater with White Slurry in Laboratory Scale

Tanning wastewater was collected from the tannery factory, Khon Kaen Tanner Group Co. Ltd., in Phon District, Khon Kaen Province. Precipitation of chromium was performed by adding white slurry of $Mg(OH)_2$ and $CaCO_3$ prepared from alkalinizing of saline groundwater. Based on the literature reviews chapter 2 (Langerwerf, 1978 and Tongchai, 1995), Cr^{3+} will be precipitated as chromium hydroxide, $Cr(OH)_3$, in the pH range between 8.5-9.0 The optimum dosage of the

$CaCO_3$ and $Mg(OH)_2$ mixture (white slurry) to precipitate Cr^{3+} from the tanning wastewater was determined in the recommended pH ranges by Jar test are described below.

- Adding the mixture of $Mg(OH)_2$ and $CaCO_3$ to a 700 ml of wastewater sample to raise the pH level to 8.5-9.0.
- Adjusting the mixing speed to 100 rpm (rapid) for 3-5 minutes and 30 rpm (slow) for another 30 minutes.
- Allowing the precipitate to settle for 6 hours.
- Analyzing the supernatant for pH, total Cr, Mg and Ca.

3.2.4 Precipitation of Chromium Tanning Wastewater with White Slurry in Model Scale

The result from the laboratory scale experiment (3.2.3) shows that chromium from the tanning wastewater could be precipitated as white slurry. Therefore, a model scale was performed to support the study by increasing the quantity of wastewater to 6,000 ml and followed the same procedure.

3.2.5 Recovery of Chromium from $Cr(OH)_3$ Precipitate

Chromium in the precipitate form of $Cr(OH)_3$ could be recovered by adding sulfuric acid, H_2SO_4 to dissolve chromium as $Cr_2(SO_4)_3$, which could be reused for tanning process. Recovery of chromium was performed as described below.

- Analyzing Cr content of the 50 ml of $Cr(OH)_3$ precipitate
- Adding H_2SO_4 to decrease the pH level to the range of 2.5-2.8.
- Analyzing the supernatant for pH and Cr.

The overall experimental procedure is shown in Figure 3.1.

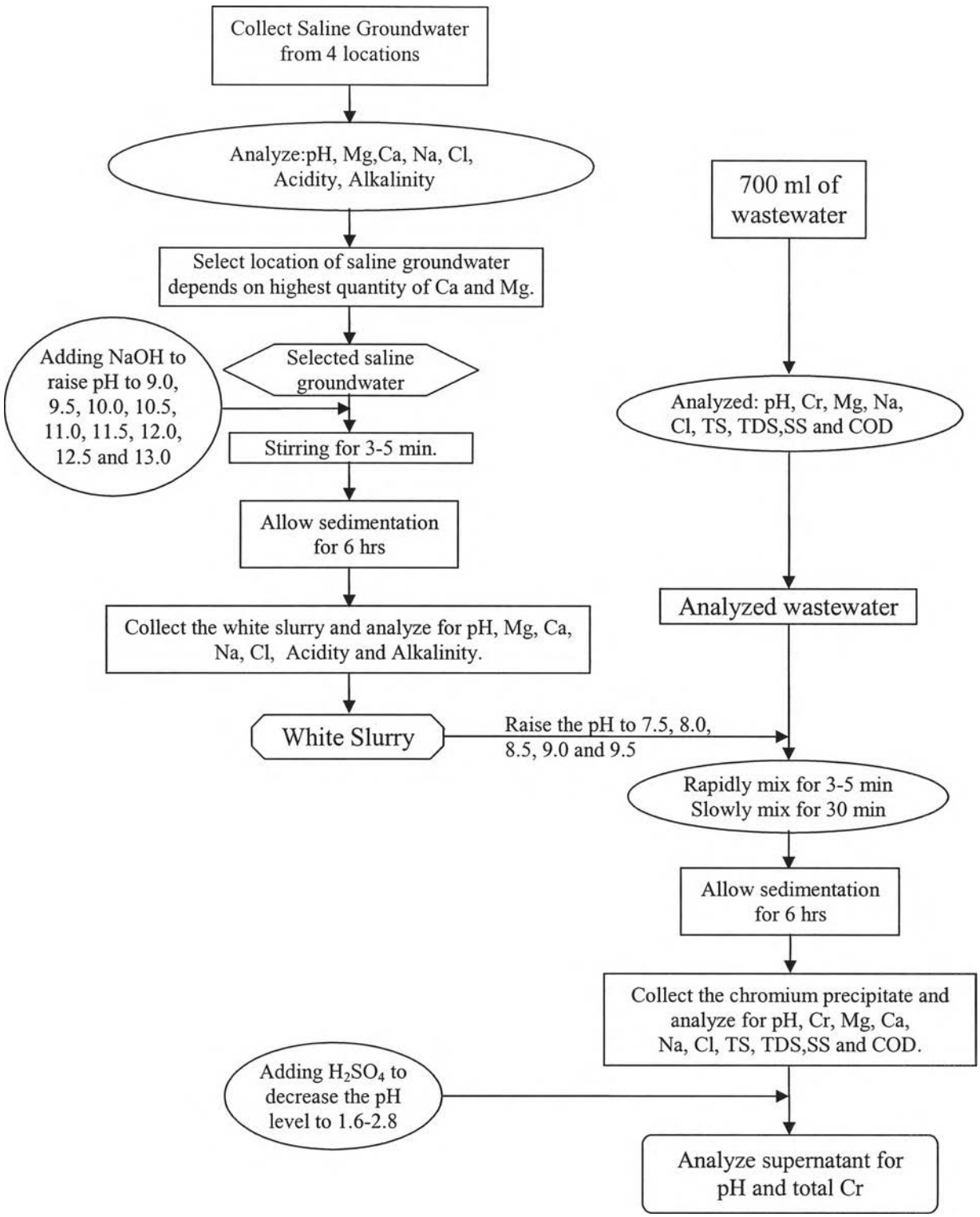

Figure 3.1 Flowchart of methodology of chromium recovery from tanning wastewater.