CHAPTER I
INTRODUCTION

1.1 Statement of the problem

Tannery industry is a leather production, which converts putrescible hides and skin into a stable and suitable material for clothing and shoes. Mostly, cow and cattle hides, are used as raw materials in the tanning process to produce leather of different qualities and properties.

The tanning process could be categorized into two categories which are chrome tanning or vegetable tanning. Both processes have different advantages and disadvantages. The chrome-tanning process requires a shorter period of time compare to the vegetable tanning process which makes it more revealing. Thus, the majority of Thailand's tanning industry; over 80% have employed the chrome tanning process.

Chemicals released from the tanning processes which are sulfide, chromium and pesticide are released with the wastewater. It was found that tannery waste was about 599 kg per ton of raw hides (Tongchai, 1995). In the developed countries, these wastes would be used as raw materials for other products such as glue and gelatin product, cattle food, pet food product, etc. On the contrary, in the developing and underdeveloped countries, tannery wastes would not be reused but instead released into the environment which is a major cause of environmental pollution. The majority of Thai's tanning factory (more than 175 factories) is settled in Tay Ban Sub district, Muang, Samutprakarn Province which is nearby the mouth of Chaopraya River. These tannery factories are divided into two groups which have their own wastewater treatment plant. These factories have the tanning capacity of 140,000 ton per year. Wastes from tanning process are in gas, liquid and solid phase. The most important waste to be considered and remediate is wastewater that contained high alkalinity concentration and high concentrated organics (BOD, COD, SS and chromium). The alkalinity concentration of waste water has a vital effect on the overall waste released since high alkalinity concentration will cause slower suspended solid sedimentation which will then allows the releasing of a greater amount of pollutant. From surveying

data of 6 Thai tanning factories it was found that the average wastewater rate was 18.2 m^3/ton of raw hides which yields the quantity of BOD, Chromium, SS and TKN of 27.54, 1.41, 40.27 and 7.16 kg/ton, respectively (Tongchai, 1995). Air pollution from the tannery process is in the form of particles, lampblack and gases such as sulfurdioxide, and hydrogensulfide. The solid wastes are meat, hair, trimmed hide, sediment and waste from the tanning process. Meat and untanned trimmed hides are sold for glue and gelatins products or pet food. Trimmed chrome-tanning leather contains high chromium which can contaminate the soil and groundwater in the landfill. Nowadays, there are some attempts to recover these chrome wastes from the tanning industry in Thailand.

Regarding with the chrome tanning process, the basic chromium oxide (Cr_2O_3) in the tanning process can produce stable hides which can endure at high temperature. Approximately 70-80% of Cr^{3+} is adhered with hides while some amount of residual Cr^{3+} are released into the wastewater. Chromium contaminated wastewater is classified as hazardous waste that cause severe impact to the environment if it is not properly treated and managed.

Chromium exists in several oxidation states (e.g. Cr^{3+} and Cr^{6+}) but only hexavalent (Cr^{6+}) and trivalent (Cr^{3+}) are biologically important. The hexavalent form is more toxic. However, a long-term exposure to trivalent form can cause allergic skin reactions and cancer (Evangelou, 1998). The toxicity of chromium is defined as chromium at 0.1 mg/g body weight. Chromium may cause a severe impact to human health such as causing lung cancer, nausea, vomiting and skin lesion. It also damages the environment by entering into the ecological system and then returned back to effect human health.

From the surveyed data, it is shown that wastewater from the tanning industry in Thailand has released 198,800 kg/year of Chromium (Tongchai, 1995). Conversing to Chrome tanning value would amount to about 28 million baht. Effluent of high Chromium wastewater after treatment has less than 2.0 mg/liter of Chromium which is then released into the environment and the majority will be collected in the sediment. Thus, the recovery of the Chromium from Chrome tanning process would save and decreases pollutant in the environment.

The removal of trivalent chromium (Cr^{+3}) can be made through the precipitation with metal hydroxide such as magnesium hydroxide and calcium hydroxide. Based on the literature reviews (Ayoub, 2001), seawater is a source of

magnesium and calcium that can be alkalinized with strong base to precipitate heavy metals. The Northeastern Region of Thailand's geology shows event of saline soil and ground water which have similar property to that of sea water. Saline groundwater is an important and inexpensive source of magnesium and calcium. It is a saturated salt solution, which contains chloride of Sodium, calcium, magnesium and water. Similar to seawater, upon an addition of sodium hydroxide (or strong base) the saline groundwater, hydroxide of magnesium and carbonate of calcium will be precipitated in the form of white slurry that can be used as alkaline agent for removal of heavy metal contaminated wastewater. Therefore, this study will employ this alkalinized saline groundwater for treatment of chromium contaminated wastewater of tannery factory.

1.2 Objectives

The main objective of this research is to recover chromium from the chrome tanning wastewater by precipitation with the alkaline reagent prepared from alkalinizing saline groundwater, and dissolution of chromium by acidification. The specific objectives are:

1. To determine the optimum pH for preparation of the alkaline reagent from saline groundwater in the form of white slurry of magnesium hydroxide and calcium carbonate by alkalinizing saline groundwater with sodium hydroxide.
2. To determine the optimum dosage of the alkaline white slurry to precipitate chromium of the chrome tanning wastewater.
3. To determine the optimum dosage of sulfuric acid to recover chromium from the precipitated chromium.

1.3 Scope of work

1. Investigation of saline groundwater sources to use as the source of alkaline reagent in the form of white slurry of magnesium hydroxide and calcium carbonate. The investigation was conducted by sampling groundwater from the nearest available salt mills in Khon Kaen, Udon Thani, Mahasarakam and Nakonratchasima Province. Groundwater source that

presented the highest concentration of calcium and magnesium would be selected for the research study.

2. Setting up the laboratory experiments for the following.
   - determination of optimum pH for preparing the alkaline white slurry by alkalinizing saline groundwater with sodium hydroxide.
   - precipitation of chromium from the chrome tanning wastewater with the alkaline white slurry. Tanning wastewater was supplied by the Khon Kaen Tanner Group Co. Ltd., in Phon District, Khon Kaen Province.
   - Recovery of chromium from the precipitated chromium by acidification with sulfuric acid.

   All of these experiments were conducted by Jar test.
3. lmplementing the findings from Jar test experiment to the Model scale experiments. Reactor of 6-liters was used for the model scale test.

   Laboratory scale and Model scale experiments were performed at the Environmental Engineering Department, Faculty of Engineering, Khon Kaen University.

1.4 Anticipated Outcomes

1. Saline groundwater could be used as the source of alkaline reagent of magnesium hydroxide and calcium carbonate for precipitating of chromium contaminant in the tanning wastewater.
2. Recovery of chromium from the precipitated chromium (chromium hydroxide) could be made by acidifying with sulfuric acid under the control of pH.