CHROMIUM RECOVERY FROM CHROME TANNING WASTEWATER USING SOLVENT EXTRACTION PROCESS

PISACHAI YOOPRASERT

A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR
THE DEGREE OF MASTER OF SCIENCE
(ENVIRONMENTAL TECHNOLOGY)
FACULTY OF GRADUATE STUDIES
MAHIDOL UNIVERSITY
2004

ISBN 974-04-4951-4

COPYRIGHT OF MAHIDOL UNIVERSITY

CHROMIUM RECOVERY FROM CHROME TANNING WASTEWATER USING SOLVENT EXTRACTION PROCESS

…………………………………………...
Mr. Pisachai Yooprasert
Candidate

…………………………………………...
Assoc. Prof. Nipapun Kungskulniti,
Dr.P.H. (Env.Health)
Major advisor

…………………………………………...
Assoc. Prof. Krisana Teankaprasith,
M.S. (Env.Health)
Co-advisor

…………………………………………...
Assoc. Prof. Suvit Shumnumsirivath,
M.S. (Env.&Water Resources Eng.)
Co-advisor

…………………………………………...
Assoc. Prof. Rassmidara Hoonsawat,
Ph.D.
Dean
Faculty of Graduate Studies

…………………………………………...
Assoc. Prof. Suvit Shumnumsirivath,
M.S.
Chair
Master of Science Programme in
Environmental Technology
Faculty of Public Health

CHROMIUM RECOVERY FROM CHROME TANNING WASTEWATER USING SOLVENT EXTRACTION PROCESS

was submitted to the Faculty of Graduate Studies, Mahidol University
for the degree of Master of Science (Environmental Technology)
on
May 26, 2004

………………………………………...
Mr. Pisachai Yooprasert
Candidate

………………………………………...
Assoc. Prof. Nipapun Kungskulniti,
Dr.P.H. (Env.Health)
Chair

………………………………………...
Assoc. Prof. Krisana Teankaprasith,
M.S. (Env.Health)
Thesis Defense Committee

………………………………………...
Assoc. Prof. Vajira Singhakajen,
M.A. (Demog.)
Thesis Defense Committee

………………………………………...
Assoc. Prof. Suvit Shumnumsirivath,
M.S. (Env.&Water Resources Eng.)
Thesis Defense Committee

………………………………………...
Assoc. Prof. Rassmidara Hoonsawat,
Ph.D.
Dean
Faculty of Graduate Studies
Mahidol University

………………………………………...
Assoc. Prof. Chalermchai Chaikittiporn,
Dr.P.H. (Epidemiology)
Dean
Faculty of Public Health
Mahidol University

ACKNOWLEDGEMENT

I wish to express my sincerest gratitude to my major advisor, Assoc. Prof. Nipapan Kungskulniti, my co-advisors, Assoc. Prof. Krisana Teankaprasith, and Assoc. Prof. Suvit Shumnumsirivath for their valuable advice, helpful guidance, and comments. I wish to thank Assoc. Prof. Vachira Singhakajen for his helpful suggestion and support in statistical analysis.

This research work is supported by the grant from the Post-Graduate Education, Training and Research Program in Environmental Science, Technology and Management under Higher Education Development Project of the Ministry of University Affairs

I also wish to thank all my friends and members of the Sanitary Engineering Department for their helpful support and encouragement.

Finally, I have to thank my parents who always stay beside and encourage me for all the time.

Pisachai Yooprasert
May, 2004

CHROMIUM RECOVERY FROM CHROME TANNING WASTEWATER USING SOLVENT EXTRACTION PROCESS

PISACHAI YOOPRASERT 4336081 PHET / M

M.Sc. (ENVIRONMENTAL TECHNOLOGY)

THESIS ADVISORS: NIPAPUN KUNGSKULNITI, Dr.P.H.(Env.Health), KRISANA TEANKAPRASITH, M.S.(Env.Health), SUVIT SHUMNUMSIRIVATH, M.S.(Env.& Water Resources Eng.)

ABSTRACT

Chromium recovery allows chromium to be reused in the chrome tanning process, is very useful for decreasing environmental problems, the process is also cost effective for leather industry. A solvent extraction process for chromium recovery, using D2EHPA (di-2-ethylhexyl phosphoric acid) as an extracting agent, was investigated in this research.

The experiment was divided into 2 stages: the extraction and recovery stage. The first stage investigated three levels of three variables: NH_3 dosage (4%, 8%, 12% v/v of D2EHPA), D2EHPA dosage (10%, 20%, 30% v/v of organic phase), and extraction time (1, 3, 6 minute[s]). In addition, three levels of two variables: HCl concentration (3.6N, 4.8N, 6.0N) and recovery time (10, 30, 60 minutes), were investigated in the recovery stage.

Results from the extraction stage showed that NH_3 dosage, D2EHPA dosage and extraction time had positive effects on chromium extraction efficiency. Statistical analysis showed the best level in the extraction stage was achieved at a NH_3 dosage of 12%, D2EHPA dosage of 30%, and extraction time of 6 minutes, which yielded an average chromium extraction efficiency of 85.88% (SD = 2.20%).

The results from the recovery stage showed that HCl concentration and recovery time had positive effects on chromium recovery efficiency. The best level in the recovery stage was achieved at 6.0N HCl and a recovery time of 30 minutes which yielded an average chromium recovery efficiency of 67.76% (SD = 1.66%).

KEY WORDS: CHROMIUM RECOVERY / TANNING WASTEWATER /
SOLVENT EXTRACTION / D2EHPA

98 pp. ISBN 974-04-4951-4

การนำกลับโครเมียมจากน้ำเสียการฟอกหนังโดยกระบวนการสกัดด้วยตัวทำละลาย
(CHROMIUM RECOVERY FROM CHROME TANNING WASTEWATER USING SOLVENT EXTRACTION PROCESS)

พิสาชัย อยู่ประเสริฐ 4336081 PHET / M

วท.ม. (เทคโนโลยีสิ่งแวดล้อม)

คณะกรรมการควบคุมวิทยานิพนธ์ : นิภาพรรณ กังสกุลนิติ, Dr.P.H.(Env.Health), กฤษณ์ เฑียรฆประสิทธิ์, M.S.(Env.Health), สุวิทย์ ชุมนุมศิริวัฒน์, M.S.(Env.&Water Resources Eng.)

บทคัดย่อ

การนำโครเมียมกลับคืนมาใช้ใหม่ในกระบวนการฟอกหนังนั้นเป็นประโยชน์อย่างยิ่งในการลดปัญหาด้านสิ่งแวดล้อม และยังเป็นการลดต้นทุนการผลิตในอุตสาหกรรมหนังสำเร็จรูป จึงได้ทำการศึกษาโดยประยุกต์กระบวนการสกัดด้วยตัวทำละลาย ซึ่งใช้ D2EHPA(di-2-ethylhexyl phosphoric acid) เป็นสารสกัด ในการนำกลับโครเมียม

การทดลองแบ่งออกเป็นสองส่วน คือ ส่วนของการสกัด และส่วนของการนำกลับ โดยส่วนของการสกัดได้ทำการศึกษาตัวแปรสามตัว ที่สามระดับ คือ ปริมาณแอมโมเนีย (4%, 8%, 12% โดยปริมาตรของ D2EHPA) ปริมาณ D2EHPA (10%, 20%, 30% โดยปริมาตรของชั้นสารอินทรีย์) และระยะเวลาสกัด (1, 3, 6 นาที) ในส่วนของการนำกลับ ได้ทำการศึกษาตัวแปรสองตัว ที่สามระดับ คือ ความเข้มข้นของกรดไฮโดรคลอริก (3.6N, 4.8N, 6.0N) และ ระยะเวลานำกลับ (10, 30, 60 นาที)

ผลการทดลองในส่วนของการสกัดแสดงให้เห็นว่า ปริมาณแอมโมเนีย ปริมาณ D2EHPA และระยะเวลาสกัด มีผลทางบวกต่อประสิทธิภาพการสกัดโครเมียม จากการวิเคราะห์ทางสถิติพบว่า การสกัดที่ระดับ ปริมาณแอมโมเนีย 12% ปริมาณ D2EHPA 30% และระยะเวลาสกัด 6 นาที จะให้ผลการสกัดโครเมียมดีที่สุดสำหรับการศึกษานี้ โดยมีประสิทธิภาพการสกัดโครเมียมเฉลี่ยถึงร้อยละ 85.88 (ค่าเบี่ยงเบนมาตรฐานร้อยละ 2.20)

ผลการทดลองในส่วนของการนำกลับแสดงให้เห็นว่า ความเข้มข้นของกรดไฮโดรคลอริก และระยะเวลานำกลับ มีผลทางบวกต่อประสิทธิภาพการนำกลับโครเมียม จากการวิเคราะห์ทางสถิติพบว่า ในการนำกลับโครเมียมที่ระดับ ความเข้มข้นของกรดไฮโดรคลอริก 6.0N และระยะเวลานำกลับ 30 นาที จะให้ผลการนำกลับโครเมียมดีที่สุดสำหรับการศึกษานี้ โดยมีประสิทธิภาพการนำกลับโครเมียมเฉลี่ยถึงร้อยละ 67.76 (ค่าเบี่ยงเบนมาตรฐานร้อยละ 1.66)

98 หน้า ISBN 974-04-4951-4

CONTENTS

CHAPTER

1 INTRODUCTION

2 LITERATURE REVIEW

CONTENTS (Continue)

CHAPTER **Page**

3 MATERIALS AND METHODS

4 RESULTS

5 DISCUSSION

6 CONCLUSIONS AND RECOMMENDATIONS

LIST OF TABLES

TABLES **Page**

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

1.1 Statement of the Problem

Leather manufacture is one of the oldest industries in human history. It is essentially a byproduct industry, utilizing hides and skins from animals raised primarily for human meat (1). Tanning industry is one of the dominant industries in Thailand. There are 176 factories in Thailand (2). Thai tanning industry has a combined annual production capacity of 150,000 tons of leather, or 15 million Sq.Ft per month (3). Whereas one ton of raw hides generates 50 m^3 of wastewater (4). Tanning industry is one of the major consumers of water that discharge large amounts of highly polluted wastewater to the environment. Its treatment is, therefore, vital for the protection of the environment. The main problems encountered in a tannery are the strong variation of the flow, load, and the high concentration of main pollutants. The biological systems cannot be applied in the same way as in the case of municipal effluents, since the main pollutants negatively affect the action of microorganisms (5).

Tanning is the process of converting animal hides and skins into leather. The resulting product has enhanced desired properties such as resistance to shrinkage in hot water, dilute acids and alkalis and does not putrefy under humid and warm conditions. The major process of the tanning industry is chrome tanning. This process utilizes chromium-containing solution with water as a carrying medium. Chromium concentration as high as 12,000 mg/L is commonly used to react with pretreated hides. The chromium source is usually a chromium oxide salt such as Cr_2O_3. In this process, 75% of the total chromium amount reacts with the hides. The remainder (25%) leaves in the waste stream in the form of tri-valent (Cr(III)) chromium ion. Cr(III) is a toxic substance, making Cr one of the most harmful pollutants in tannery waste streams. Chromium also affects air and ground quality. It can be transferred in aerosol form, significant distances from its emission point giving rise to human health concerns(1).

Chromium recovery allows chromium to be reused in the chrome tanning process, is very useful for decreasing environmental problems, the process is also cost effective for leather industry. Solvent extraction using organophosphorus acid derivatives as an extracting reagent, is the new method to remove or recover large number of metals, including chromium. Di-2-ethylhexyl phosphoric acid (D2EHPA) is one of the organophosphorus acid derivatives, widely used in metal recovery and reported by several investigators (6, 7, 8, 9).

The solvent extraction method for chromium recovery using D2EHPA was focused in this research, which could be applied as an alternative approach to recover chromium from tannery wastewater.

1.2 Research Objectives

1.2.1 Main Objective

To investigate the chromium recovery from tannery wastewater using the solvent extraction technique.

1.2.2 Specific Objectives

1.2.2.1 Specific Objectives in Extraction Stage

1) To investigate chromium extraction efficiencies at different doses of NH_3: 4, 8, 12% v/v of D2EHPA.

2) To investigate chromium extraction efficiencies at different doses of D2EHPA: 10, 20, 30% v/v of organic phase.

3) To investigate chromium extraction efficiencies at different extraction times: 1, 3, 6 minute(s).

1.2.2.1 Specific Objectives in Recovery Stage

1) To investigate chromium recovery efficiencies at different concentrations of HCl: 3.6, 4.8, 6.0 N.

2) To investigate chromium recovery efficiencies at different recovery times: 10, 30, 60 minutes.

1.3 Research Hypotheses

1.3.1 Research Hypotheses in Extraction Stage

1) In extraction stage of solvent extraction process, the chromium extraction efficiency at NH_3 dose of 12% v/v of D2EHPA is better than those of 8% and 4%.

2) In extraction stage of solvent extraction process, the chromium extraction efficiency at D2EHPA dose of 30% v/v of organic phase is better than those of 20% and 10%.

3) In extraction stage of solvent extraction process, the chromium extraction efficiency at extraction time of 6 minutes is better than those of 3 and 1 minute(s).

1.3.2 Research Hypotheses in Recovery Stage

1) In recovery stage of solvent extraction process, the chromium recovery efficiency at concentration of 6.0N HCl is better than those of 4.8N and 3.6N.

2) In recovery stage of solvent extraction process, the chromium recovery efficiency at recovery time of 60 minutes is better than those of 30 and 10 minutes.

1.4 Research Variables

1.4.1 Dependent Variables

1.4.1.1 Dependent Variable in Extraction Stage

- Chromium extraction efficiency.

1.4.1.2 Dependent Variable in Recovery Stage

- Chromium recovery efficiency.

1.4.2 Independent Variables

1.4.2.1 Dependent Variable in Extraction Stage

1) NH_3 dosage: 4, 8, 12% v/v of D2EHPA.
2) D2EHPA dosage: 10, 20, 30% v/v of organic phase.
3) Extraction time: 1, 3, 6 minute(s).

1.4.2.2 Dependent Variable in Extraction Stage

1) HCl concentration: 3.6, 4.8, 6.0 N.
2) Recovery time: 10, 30, 60 minutes.

1.4.3 Control Variables

1) Settling time: 30 minutes.
2) 1-Decanol dosage: 10% v/v of organic phase.

1.5 Scope of the Study

1) Chrome tanning wastewater was obtained from a tannery factory located in Samutprakarn province.

2) Solvent extraction technique, using D2EHPA as extracting agent, was selected to recover chromium from chrome tanning wastewater.

3) Experiments divided into two stages, extraction stage and recovery stage.

4) NH_3 dosage , D2EHPA dosage, and extraction time were investigated in extraction stage.

5) In extraction stage, pH of the chrome tanning wastewater (aqueous phase) was in the range of 2-3, 1-decanol was used as emulsifier, and coconut oil was used as solvent.

6) HCl concentration and recovery time were investigated in recovery stage.

7) In recovery stage, both the organic phase and aqueous phase were not adjusted for pH.

8) Batch lab-scale apparatuses were assembled and conducted at the laboratory of Environmental Technology Program, Department of Sanitary Engineering, Faculty of Public Health, Mahidol University.

1.6 Definition of Keywords

1) Solvent Extraction Technique: The isolation or purification technique is the physical process, using the difference of the solubility of the desired compound in the various solvents.

2) NH_3 Dosage: The desired dose of NH_3 was used in chromium extraction stage.

3) D2EHPA Dosage: The desired dose of D2EHPA was used in chromium extraction stage.

4) Extraction Time: The shaking time at 150rpm in chromium extraction stage that chromium in chrome tanning wastewater was extracted by D2EHPA.

5) HCl Concentration: The desired concentration of HCl acid was used in chromium recovery stage.

6) Recovery Time: The shaking time at 150rpm in chromium recovery stage that chromium in organic phase was recovered by HCl acid.

7) Chromium Extraction Efficiency: The capability of extracted chromium in chromium extraction stage from the chrome tanning wastewater, express in term of percentage as follows :

$$\text{Extraction Efficiency (\%)} = \frac{(\text{initial Cr concentration} - \text{final Cr concentration}) \text{ x } 100}{\text{initial Cr concentration}}$$

8) Chromium Recovery Efficiency: The capability of recovered chromium in chromium recovery stage from the organic phase obtained from chromium extraction stage, express in term of percentage as follows :

$$\text{Recovery Efficiency (\%)} = \frac{\text{final Cr concentration x } 100}{\text{initial Cr concentration}}$$

1.7 Conceptual Framework

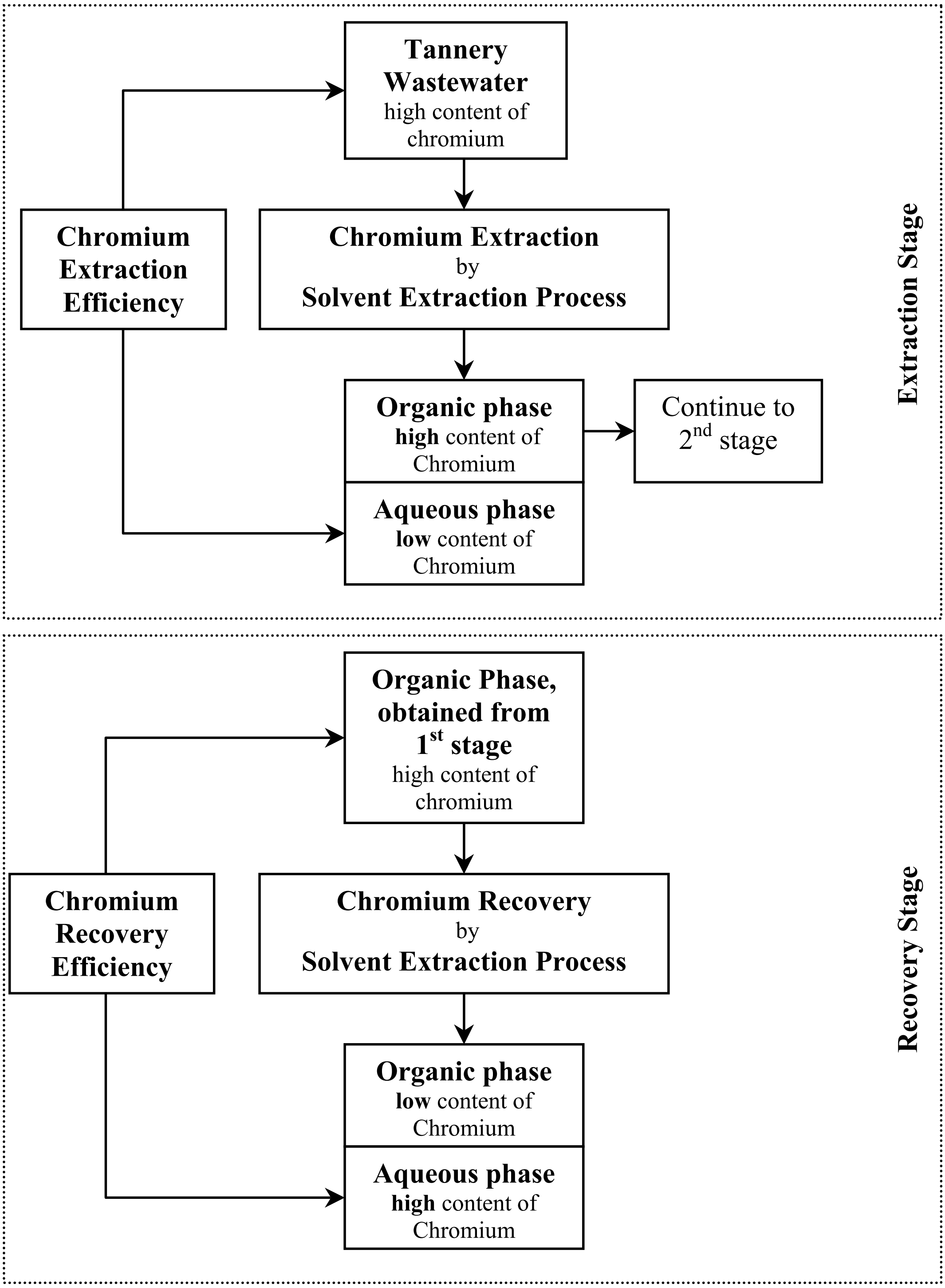


Figure 1-1 Conceptual Framework

CHAPTER 2
LITERATURE REVIEW

2.1 Tannery Process (10)

Leather tanning is the process of converting raw hides or skins into leather. Hides and skins have the ability to absorb tannic acid and other chemical substances that prevent them from decaying, make them resistant to wetting, and keep them supple and durable. The surface of hides and skins contains the hair and oil glands and is known as the grain side. The flesh side of the hide or skin is much thicker and softer. The three types of hides and skins most often used in leather manufacture are from cattle, sheep, and pigs.

Tanning is essentially the reaction of collagen fibers in the hide with tannins, chromium, alum, or other chemical agents. The most common tanning agents used in the U. S. are trivalent chromium and vegetable tannins extracted from specific tree barks. Alum, syntans (man-made chemicals), formaldehyde, glutaraldehyde, and heavy oils are other tanning agents.

"Leather tanning" is a general term for the numerous processing steps involved in converting animal hides or skins into finished leather. Production of leather by both vegetable tanning and chrome tanning is described below. Chrome tanning accounts for approximately 90 percent of U.S. tanning production. Figure 2-1 presents a general flow diagram for the leather tanning and finishing process. Trimming, soaking, fleshing, and unhairing, the first steps of the process, are referred to as the beamhouse operations. Bating, pickling, tanning, wringing, and splitting are referred to as tanyard processes. Finishing processes include conditioning, staking, dry milling, buffing, spray finishing, and plating.

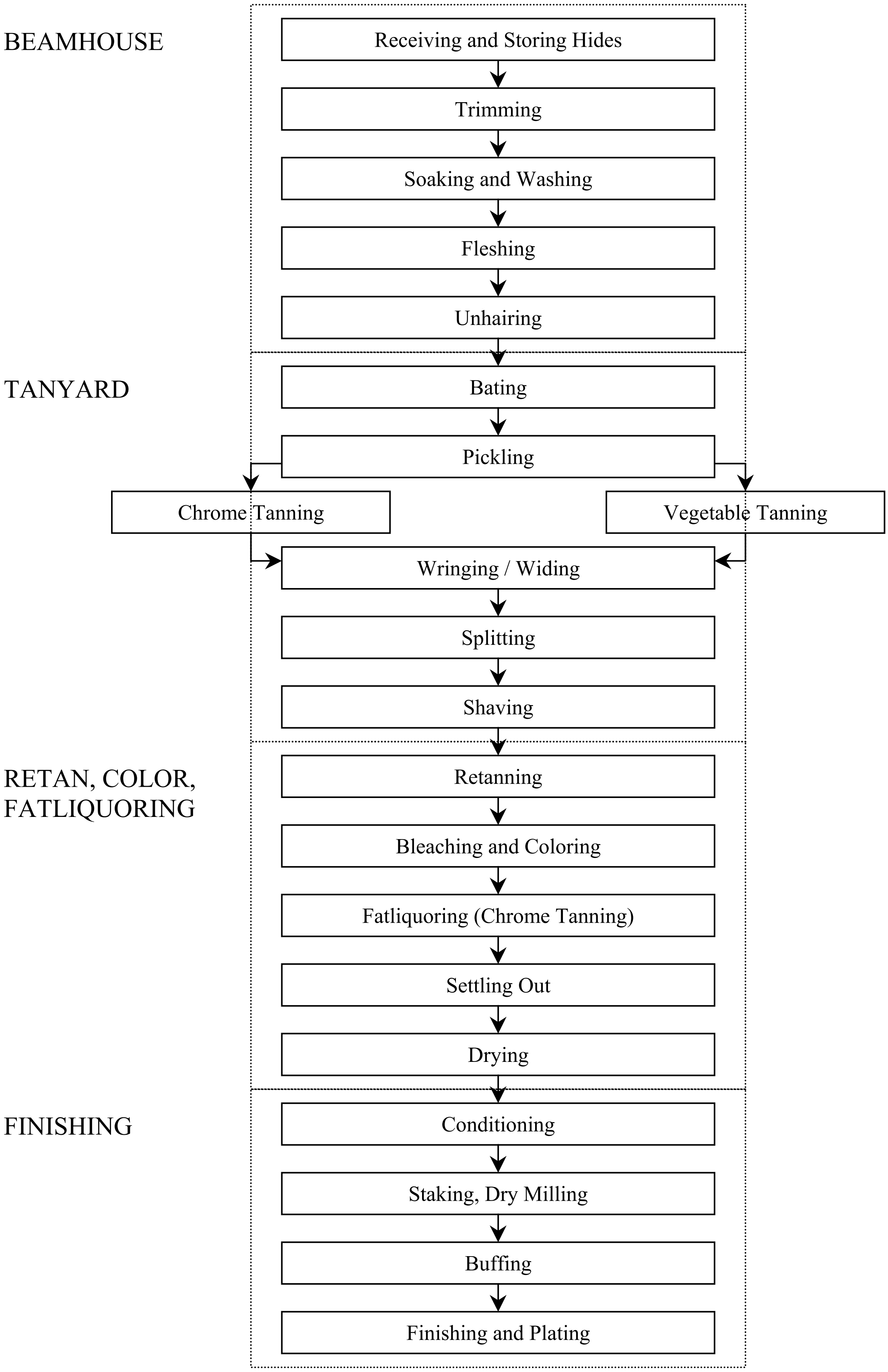


Figure 2-1 General Flow Diagram for Leather Tanning and Finishing Process

2.1.1 Vegetable Tanning

Heavy leathers and sole leathers are produced by the vegetable tanning process, the oldest of any process in use in the leather tanning industry. The hides are first trimmed and soaked to remove salt and other solids and to restore moisture lost during curing. Following the soaking, the hides are fleshed to remove the excess tissue, to impart uniform thickness, and to remove muscles or fat adhering to the hide. Hides are then dehaired to ensure that the grain is clean and the hair follicles are free of hair roots. Liming is the most common method of hair removal, but thermal, oxidative, and chemical methods also exist. The normal procedure for liming is to use a series of pits or drums containing lime liquors (calcium hydroxide) and sharpening agents. Following liming, the hides are dehaired by scraping or by machine. Deliming is then performed to make the skins receptive to the vegetable tanning. Bating, an enzymatic action for the removal of unwanted hide components after liming, is performed to impart softness, stretch, and flexibility to the leather. Bating and deliming are usually performed together by placing the hides in an aqueous solution of an ammonium salt and proteolytic enzymes at 27 °C to 32 °C (80°F to 90°F). Pickling may also be performed by treating the hide with a brine solution and sulfuric acid to adjust the acidity for preservation or tanning.

In the vegetable tanning process, the concentration of the tanning materials starts out low and is gradually increased as the tannage proceeds. It usually takes 3 weeks for the tanning material to penetrate to the center of the hide. The skins or hides are then wrung and may be cropped or split; heavy hides may be retanned and scrubbed. For sole leather, the hides are commonly dipped in vats or drums containing sodium bicarbonate or sulfuric acid for bleaching and removal of surface tannins. Materials such as lignosulfate, corn sugar, oils, and specialty chemicals may be added to the leather. The leather is then set out to smooth and dry and may then undergo further finishing steps. However, a high percentage of vegetable-tanned leathers do not undergo retanning, coloring, fatliquoring, or finishing.

Leather may be dried by any of five common methods. Air drying is the simplest method. The leather is hung or placed on racks and dried by the natural circulation of air around it. A toggling unit consists of a number of screens placed in a dryer that has controlled temperature and humidity. In a pasting unit, leathers are pasted on large sheets of plate glass, porcelain, or metal and sent through a tunnel dryer with several controlled temperature and humidity zones. In vacuum drying, the leather is spread out, grain down, on a smooth surface to which heat is applied. A vacuum hood is placed over the surface, and a vacuum is applied to aid in drying the leather. High-frequency drying involves the use of a high frequency electromagnetic field to dry the leather.

2.1.2 Chrome Tanning

Chrome-tanned leather tends to be softer and more pliable than vegetable-tanned leather, has higher thermal stability, is very stable in water, and takes less time to produce than vegetable-tanned leather. Almost all leather made from lighter-weight cattle hides and from the skin of sheep, lambs, goats, and pigs is chrome tanned. The first steps of the process (soaking, fleshing, liming/dehairing, deliming, bating, and pickling) and the drying/finishing steps are essentially the same as in vegetable tanning. However, in chrome tanning, the additional processes of retanning, dyeing, and fatliquoring are usually performed to produce usable leathers and a preliminary degreasing step may be necessary when using animal skins, such as sheepskin.

Chrome tanning in the United States is performed using a one-bath process that is based on the reaction between the hide and a trivalent chromium salt, usually a basic chromium sulfate. In the typical one-bath process, the hides are in a pickled state at a pH of 3 or lower, the chrome tanning materials are introduced, and the pH is raised. Following tanning, the chrome tanned leather is piled down, wrung, and graded for the thickness and quality, split into flesh and grain layers, and shaved to the desired thickness. The grain leathers from the shaving machine are then separated for retanning, dyeing, and fatliquoring. Leather that is not subject to scuffs and scratches can be dyed on the surface only. For other types of leather (i. e., shoe leather) the dye must penetrate further into the leather. Typical dyestuffs are aniline-based compounds that combine with the skin to form an insoluble compound.

Fatliquoring is the process of introducing oil into the skin before the leather is dried to replace the natural oils lost in beamhouse and tanyard processes. Fatliquoring is usually performed in a drum using an oil emulsion at temperatures of about 60^0 to 66^0C (140^0 to 150^0F) for 30 to 40 minutes. After fatliquoring, the leather is wrung, set out, dried, and finished. The finishing process refers to all the steps that are carried out after drying.

2.1.3 Leather Finishing

Leathers may be finished in a variety of ways: buffed with fine abrasives to produce a suede finish; waxed, shellacked, or treated with pigments, dyes, and resins to achieve a smooth, polished surface and the desired color; or lacquered with urethane for a glossy patent leather. Water-based or solvent-based finishes may also be applied to the leather. Plating is then used to smooth the surface of the coating materials and bond them to the grain. Hides may also be embossed.

2.1.4 Chromium Recovery in Tannery

There are 3 ways to recover and reuse chromium.

1) Direct Reuse

The effluent from tanning is direct reused by adding more chromium enough to reuse. The advantages of this way are salt and any impurity will be accumulated in the reused solution that reduces the leather quality.

2) Indirect Reuse

Chromium in the effluent is precipitated into hydroxyl form. This sediment will be dissolved by sulfuric acid. This cleaner chromium solution that received from this way can be reused. Efficiency and quality leather can be achieved.

3) Chromium Separation

Chromium in the effluent is separated by any complicated technique such as electrodialysis, membrane separation or ion exchange. The cleanest chromium solution can be achieved from this way but not cost effective when compare with indirect reuse.

2.2 Tannery Wastewater Characteristics

The Figure 2-2 shows all the losses along the tanning process: for 1000 kg of raw material, only 200 kg of finished leather is produced. This data gives a good scheme of the amount of wastes involved. It gives an outline of the focal pollution: the overall flows of aqueous effluents and solid wastes are evaluated.

The principle pollutants in wastewater discharges are from the beamhouse operations and the subsequent tanning operations. The wastewater is rich in organic substances, solids and dissolved substances and it is extremely polluting.

Beamhouse flows contain high levels of suspended solids and dissolved organic matter, curing salt and grease, in addition to unused process chemicals (particularly dissolved sulfides); they will also be alkaline and will have a high oxygen demand.

Tanning produces acidic effluents which when derived from chrome tanning will contain unused trivalent chromium salts. Typically, approximately 25% of the applied charge of chromium salt is discharged on completion of the tanning operation.

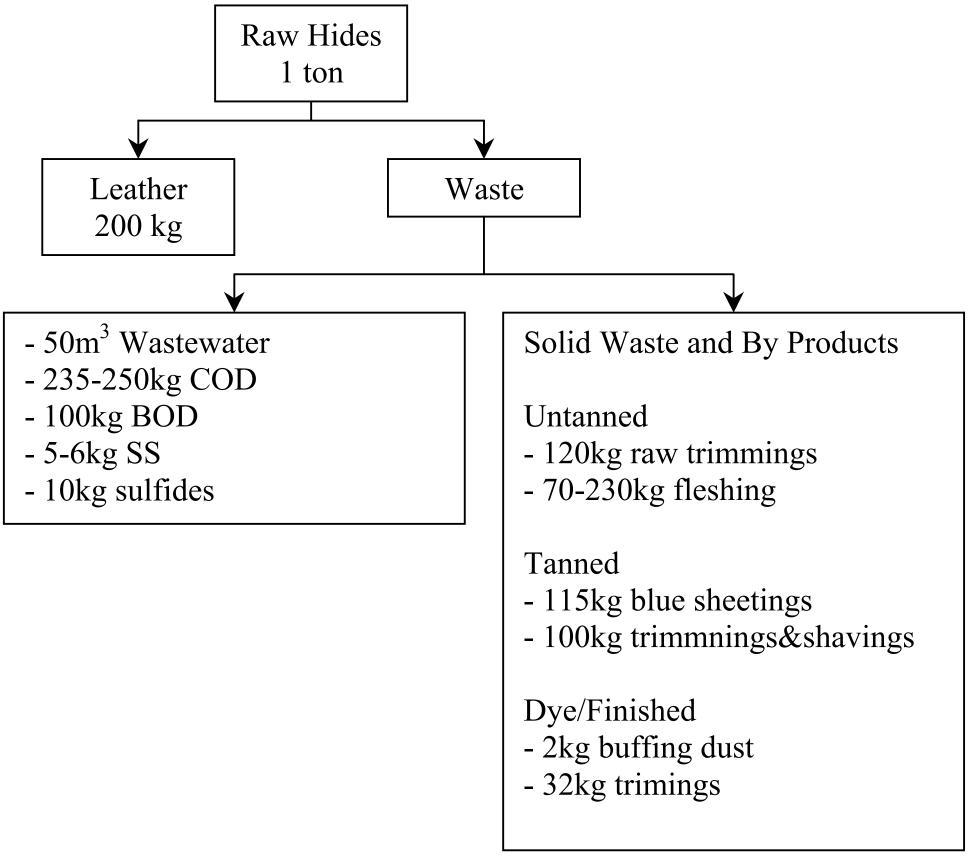


Figure 2-2 The Ratio of Input of Raw Hide, output of Leather and Waste (4)

The following Table 2-1 demonstrates the characteristics of wastewater as combined in the general tannery process with summary data.

Table 2-1 The Composition of Tanning Liquor Characteristics from Tanneries

Parameters	Source				
	Pakistan (11)	Italy (12)	Greece (13)	Thailand (14)	India, Kanpur (15)
pH	3.34	3.7-4.2	4	2.93^{a}, 3.56^{b}	2.6^{*}, 3.7^{**}
TS	91878	700-2900	NA	86850^{a}, 131670^{b}	59900^{*}, 96600^{**}
TDS	91710	NA	22400	85570^{a}, 129170^{b}	58700^{*}, 76500^{**}
Suspend S.	146	NA	6200	1280^{a}, 2510^{b}	1160^{*}, 16800^{**}
Sulphides	32000	NA	385	NA	279^{*}, 47^{**}
Sulphates	240	22000-23000	NA	NA	NA
TKN	118	1070-1110	520	450^{a}, 810^{b}	NA
Phosphate	2	NA	NA	NA	NA
Chlorides	28991	11000-16000	18500	24900^{a}, 45280^{b}	9630^{*}, 13900^{**}
BOD	480	NA	1720	NA	1390^{*}, 750^{**}
COD	2080	8600	8540	4030^{a}, 5500^{b}	2240^{*}, 1350^{**}
Total Chromium	6132	360	3500	2170^{b}, 4130^{a}	600^{*}, 1060^{**}
Flow Rate (m^3/d)	28-120	8-20	60	40	80-120

Remarks: All values are in mg/l except pH

* Winter in Kanpur in January – February 1997

** Summer in Kanpur in May – June 1996

a Tanning liquor without additive agent

b Tanning liquor with additive agent

Another environmental impact, which cannot be easily resolved in tannery wastewater, is salinity, it's reaching conductivity values on the order of 10,000–12,000 μs/cm. The main contribution to the effluent salinity is derived from the salt used for the preservation of the skins after flaying, followed by the high salinity of the pickling baths (preparation of skins with salts and acids prior to the addition of the tanning agent) and the tanning stage. Therefore, 30% of the chlorides contained in the effluent come from the pickling bath, and 60% of the sulfates come from the tanning bath (13).

2.3 Treatment Methods of Tannery Wastewater

Tannery wastewater represents a powerful pollutant, mainly because of their high CODs and elevated chrome contents. Considering the large amount and the low biodegradability of various chemicals, tannery wastewater treatment represents a serious environmental and technological problem (16). The presence of chromium in the effluent is a major concern for the tanning industry. Currently, chemical precipitation methods are practiced for the removal of chromium from the effluent, but that leads to the formation of chrome-bearing solid wastes. The other membrane separation and ion exchange methods available are unfeasible due to their cost (17).

Biological alternatives were studied on tannery wastewater treatment. Bioaccumulation is one of them, using brown seaweed *Sargassum wightii* (17). The results show that at a pH of 3.5 - 3.8 for 6 hours duration gave the maximum chromium uptake of about 83%. The *Sargassum* species exhibited a maximum uptake of 35 mg chromium per gram of seaweed, and when the quantity of *Sargassum* species is increased from 0.25 to 0.5 g, the chromium uptake increases from 71 to 84%. An aerobic process for the treatment of tannery wastewater was also studied (5). The level of chromium in the produced sludge and the treated wastewater were evaluated. The results revealed that the aerobic treatment improved the chemical oxidation demands (COD) of the wastewater. Chromium was eliminated in the wastewater by 46.3%. The levels of the other metal were also reduced with a range of elimination from 19% for Zinc to 58% for Manganese. Nevertheless, the concentrations of Chromium both in treated wastewater and sludge exceeded the permissible level.

Another several techniques were adapted into tannery wastewater treatment processes. The biological degradation carried out in sequencing batch biofilm reactor (SBBR), is combined with oxidation by ozone (18). SBBR performances with and without ozonation were compared with very satisfactory results when COD, TKN, and TSS removal efficiencies were 96%, 92%, and 98%, respectively. Whereas membrane sequencing batch reactor (MSBR) technique is able to achieve the removal efficiencies close to 100% in ammonium and 90% in COD while the TN removal efficiency ranged from 60 to 90% for wastewater coming out from the beamhouse section of a tannery process (19). The wastewater, produced after the oxidation of sulphide compounds, contained average COD and ammonium concentrations of 550 and 90mg/L respectively. The system was operated for a period of 150 days, with no sludge removal during the whole period of operation. The biomass concentration inside the reactor varied considerably, with maximum values close to 10g/L at the end of operation. Low biomass yield values were achieved probably due to the low feed/microorganisms (F/M) ratio. An important accumulation of organic matter in the reactor was noticed, although the COD effluent was not affected due to the permeation through the membrane.

2.4 Chemistry of Chromium (20)

Chromium (C.A.S. 7440-47-3) is an odorless, hard, steel-gray, lustrous metal available in crystals or powder. It has several different forms, the most common of which are the metal, chromium (0); chromium (III) compounds; and chromium (VI) compounds. Chromium (III) occurs naturally in the environment: types (0) and (VI) are produced by industrial processes.

Chromium is used as an alloying and plating element on metal and plastic substrates for corrosion resistance in chromium-containing and stainless steels, and in protective coatings for automotive and equipment accessories. It is also used in nuclear and high temperature research.

Trivalent chromium compounds (III) include chromic oxide (Cr_2O_3); chromium acetate ($Cr[CH_3COO]_3{\cdot}H_2O$); chromium nitrate ($Cr[NO_3]_3{\cdot}9H_2O$); chromium chloride ($CrCl_3$); ferrochromite ($FeCr_2O_4$); chromium phosphate ($CrPO_4$); chromium sulfate ($Cr_2[SO_4]_3$); and sodium chromite ($NaCrO_2$). Hexavalent chromium compounds (VI) include ammonium dichromate ($[NH_4]_2Cr_2O_7$); barium chromate ($Ba{\cdot}CrH_2O_4$); calcium chromate ($CaCrO_4$); chromium trioxide (CrO_3); lead chromate ($PbCrO_4$); sodium dichromate ($Na_2Cr_2O_7{\cdot}2H_2O$); strontium chromate ($SrCrO_4$); potassium chromate (K_2CrO_4); potassium dichromate ($K_2Cr_2O_7$); sodium chromate

(Na_2CrO_4); and zinc chromate ($ZnCrO_4$). Other compounds include chromium carbonate ($Cr[CO_3]_3$) and lead chromate oxide ($CrO_4Pb{\cdot}OPb$).

Chromium and its compounds are used in refractories, drilling muds, electroplating cleaning agents in the metal finishing industry, mordants in the textile industry, catalytic manufacture, fungicides and wood preservatives, and in the production of chromic acid and specialty chemicals. They are also used as a constituent of inorganic pigments, and as a sensitizer in the photographic industry. Chromium compounds are used as dyes and pigments and in medicinal astringents and antiseptics. Other uses for chromium and its compounds include organic chemical synthesis, leather treatment, photomechanical processing, and industrial water treatment, including treatment of cooling tower water.

Chromium trioxide is used for metal plating and treatment, wood treatment and preservative, and in the manufacture of chromated copper arsentate. Chromium acetate, sodium chromate and potassium chromate are used in the tanning and textile industries.

Chromium is insoluble in hot and cold water, nitric acid, and aqua regia, but is soluble in diluted sulfuric acid and hydrochloric acid. Barium chromate is insoluble in both cold and hot water but is soluble in mineral acid and acids. Chromic oxides are soluble in cold water, but insoluble in alcohol; acrid smoke and irritating fumes are emitted when it is heated to decomposition. Chromium carbonate is soluble in water containing carbon dioxide, but insoluble in alcohol. Chromium phosphate is slightly soluble in cold water, soluble in acids and alkalies, and insoluble in acetic acid.

Chromium trioxides are soluble in alcohol, ethanol, sulfuric acid, and nitric acid; when heated to decomposition, chromium trioxides emit smoke and irritating fumes. Lead chromate is insoluble in water, acetic acid, and ammonia, but is soluble in acid and alkali; when heated to decomposition, emits toxic fumes of lead. Potassium chromate and potassium dichromate are soluble in cold and hot water and insoluble in alcohol. Sodium chromed is soluble in cold water and methanol, and only slightly soluble in alcohol. Sodium dichromate is soluble in cold and hot water and insoluble in alcohol; toxic fumes of sodium monoxide are emitted when this compound is heated to decomposition. Strontium chromate is soluble in cold and hot water, hydrochloric acid, nitric acid, acetic acid, and ammonium salts. Zinc chromate is insoluble in cold water and acetone, dissolves in hot water, and is soluble in acid and liquid ammonia.

2.5 Toxicity of Chromium (20, 21)

Chromium can exposed to human by breathing air, drinking water, or eating food containing chromium or through skin contact with chromium or chromium compounds. The level of chromium in air and water is generally low. The concentration of total chromium in air (both chromium (III) and chromium (VI)) generally ranges between 0.01 and 0.03 microgram (µg) (1 µg equals 1/1,000,000 of a gram) per cubic meter of air ($\mu g/m^3$). Chromium concentrations in drinking water (mostly as chromium (III)) are generally very low, less than 2 parts of chromium in a billion parts of water (2 ppb). Contaminated well water may contain chromium (VI). For the general population, eating foods that contain chromium is the most likely route of chromium (III) exposure. Chromium (III) occurs naturally in many fresh vegetables, fruits, meat, yeast, and grain. Various methods of processing, storage, and preparation can alter the chromium content of food. Acidic foods in contact with stainless steel cans or cooking utensils might contain higher levels of chromium because of leaching from stainless steel. Refining processes used to make white bread or sugar can decrease chromium levels. Chromium (III) is an essential nutrient for humans. On the average, adults in the United States take in an estimated 60 µg of chromium daily from food. People may also be exposed to chromium from using consumer products such as household utensils, wood preservatives, cement, cleaning products, textiles, and tanned leather.

Chromium and certain chromium compounds are classified as substances known to be carcinogenic, according to the National Toxicology Program's Fifth Annual Report on Carcinogens. In the national Toxic Release Inventory, EPA classifies chromium as a "de minimis" carcinogen, meaning that the minimum amount of the chemical set by OSHA is considered to be carcinogenic.

Chromium compounds vary greatly in their toxic and carcinogenic effects. Trivalent chromium compounds are considerably less toxic than the hexavalent compounds and are neither irritating nor corrosive. There is inadequate evidence for carcinogenicity of chromium oxide, and chromium acetate. There is sufficient evidence for carcinogenicity of barium chromate, calcium chromate, chromium trioxide, lead chromate, sodium dichromate, and strontium chromate. These compounds have not been evaluated for their carcinogenicity: chromium carbonate, chromium phosphate, cobalt chromium alloy, lead chromate oxide, potassium chromate, potassium dichromate, sodium chromate, and zinc chromate.

The major acute effort from ingested chromium is acute renal tubular necrosis. Exposure to chromium, particularly in the chrome production and chrome pigment industries, is associated with cancer of the respiratory tract. Hexavalent chromium compounds are corrosive and cause chronic ulceration and perforation of the nasal septum. They also cause chronic ulceration of other skin surfaces. The general populations can be exposed to chromium through the air, water, soils, and food.

2.6 Solvent Extraction Process (22)

Extraction is the physical process by which a compound (or a mixture of compounds) is transferred from one phase into another. The isolation of trimyristin form nutmeg is an example of a solid-liquid extraction. It is also possible to partition the components of a mixture between two immiscible liquids (i.e., liquids that will not dissolve in each other and form two distinct phases when combined). This process is called a liquid-liquid extraction.

There are two general types of liquid-liquid extractions:

1) An organic solvent extraction, in which an organic solvent with a high affinity for the desired compound is used to extract the compound from another solution, and

2) An acid-base extraction, in which an organic acid or base is extracted from an organic solvent by using an aqueous solution of an inorganic base or acid, respectively. A neutralization occurs which converts the compound into an ionic, water-soluble salt, causing it to transfer from the organic phase to the aqueous phase.

2.6.1 Extraction with Organic Solvents

Liquid-liquid extractions usually involve water and an organic solvent. Most common organic solvents (diethyl ether, ethyl acetate, toluene, methylene chloride) are immiscible in water. If you place 50 ml of ethyl acetate and 50 ml of water in a flask and stir the solution to mix it, you will not obtain a homogeneous solution. Rather, if the solution is allowed to stand after stirring, two distinct liquid phases will form in the flask: the more dense solvent as the lower layer and the less dense solvent as the upper layer.

Most organic solvents are much less polar than water. A general rule of thumb for solubility states that **like dissolves like**. Polar compounds are more soluble in polar solvents than in nonpolar solvents, and vice versa. The selective solubility of different compounds in polar versus nonpolar solvents allows the separation of the compounds in a mixture by liquid-liquid extraction.

Suppose that we add a compound X to a flask containing ethyl acetate and water, and stir the contents of the flask to mix them. After mixing, the ethyl acetate and water will separate into two distinct phases, and compound X will be found dissolved in both the ethyl acetate layer and in the water layer. How compound X distributes between the two solvents is based on the solubility of X in each of the two solvents: more of compound X will be found in the solvent in which it is more soluble. The ratio of the concentrations of X in each of the immiscible solvents is called the distribution coefficient or the partition coefficient, K_d, where

$$[X]_{water} \overset{K_d}{\rightleftharpoons} [X]_{ethyl\ acetate}$$

$$K_d = \frac{\text{concentration of X in ethyl acetate layer}}{\text{concentration of X in water layer}}$$

The value of the distribution coefficient depends on the solubility of the compound in the two solvents in the system. In the above system, if compound X has a higher solubility in ethyl acetate than in water, at equilibrium the concentration of X in ethyl acetate will be greater than the concentration of compound X in water, and the value of the distribution coefficient K_d will be greater than 1. If instead compound X has a higher solubility in water than in ethyl acetate, at equilibrium the concentration of X in water will be greater than the concentration of compound X in ethyl acetate, and the value of the distribution coefficient K_d will be less than 1.

The efficiency of a liquid-liquid extraction depends on the distribution coefficient of the desired compound between the two solvents. If we want to extract an organic compound from an aqueous solution into an organic solvent, it is desirable to use a solvent that has a much higher affinity for the compound than does water. For example, at 25 ^{o}C, the solubility of benzoic acid in water is 3.4 g per liter while the solubility of benzoic acid in chloroform ($CHCl_3$) is 222 g per liter. Water and chloroform are immiscible solvents. If a solution of 1 g of benzoic acid in 400 ml of water is extracted with 400 ml of chloroform, we would expect most of the benzoic acid to be transferred to the chloroform layer in which it is more soluble. The benzoic acid will distribute itself between the two solvents in the ratio of the solubilities in each solvent:

$$K_d = \frac{\text{222g/l in chloroform layer}}{\text{3.4 g/l in water layer}} = 65.3$$

No matter how much benzoic acid is present in the system, it will always be distributed between the chloroform and water so that the ratio of the concentration in each solvent is 65.3.

From this estimate of the distribution coefficient, we can calculate how much benzoic acid is present in the chloroform and water layers after the extraction. Let x = grams of benzoic acid in the water layer and y = grams of benzoic acid in the chloroform layer. Since we started with 1 g of benzoic acid, so x + y = 1. Using this equation along with the value for the distribution coefficient calculated above, we can determine the concentration of benzoic acid in each layer:

$$K_d = \frac{\text{x g in 400ml chloroform}}{\text{y g in 400ml water}} = 65.3$$

or, since the volumes of both solvents used are the same:

$$\frac{x}{y} = 65.3$$

The total amount of benzoic acid present is (x + y) = 1. Rearranging this equation and substituting for x in the previous equation gives

$$\frac{y - 1}{y} = 65.3$$

Solving this equation for y gives 0.015 g (15 mg) of benzoic acid in the water layer, and, since the total amount of benzoic acid is 1 g, there is 0.985 g (985 mg) of benzoic acid in the chloroform layer.

2.6.2 Multiple Extractions

In the previous example, one extraction with 400 ml of chloroform removed 98.5 % of the benzoic acid from the aqueous solution. If we divide the 400 ml of chloroform used in half and do two successive extractions of the aqueous phase, the amount of benzoic acid extracted will increase.

The equation for the distribution coefficient for two 200 ml chloroform extractions of the 400 ml aqueous solution of benzoic acid is

$$K_d = \frac{\text{x g in 200ml chloroform}}{\text{y g in 400ml water}} = 65.3$$

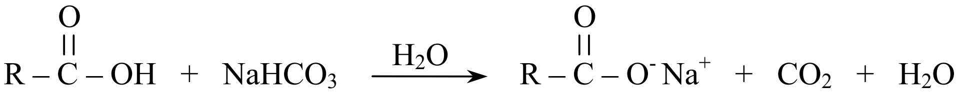
In the first extraction, 1 g of benzoic acid is distributed between the phases, so (x + y) = 1 as before. Solving the two equations in two unknowns gives x = 0.97 (g in $CHCl_3$) and y = 0.03 (g in H_2O). When the aqueous phase is extracted a second time with a fresh 200 ml of chloroform, only 0.03 g of benzoic acid is left in the aqueous phase to distribute between the two solvents. In this extraction the equation for the distribution coefficient is the same but (x + y) = 0.03, and solving for x and y, the amount of benzoic acid in each layer after the second extraction gives x = 0.0291 (g in $CHCl_3$) and y = 0.0009 (g in H_2O). Combining the amounts of benzoic acid found in the two chloroform extracts gives 99.91% (0.9991 g of the original 1 g) of the benzoic acid extracted into the chloroform layer by using two 200 ml extractions instead of 98.5% removed with one 400 ml extraction. In general, it is always more efficient to carry out several extractions using a small volume of solvent each time than to carry out a single extraction using a large volume of solvent.

2.6.3 Acid-Base Extraction

Organic compounds are classified as being neutral, acidic, or basic depending on the types of functional groups they contain. Many organic compounds, although just slightly polar overall, contain functional groups that can act as a Brø nsted-Lowry acid or base (i.e., they can donate or accept a proton, respectively). Carboxylic acids, phenols, and thiols are examples of acidic functional groups;

substituted amines (including anilines) are examples of basic functional groups. Although the water-solubility of these compounds is often limited because of their overall nonpolar character, their aqueous solubilities can be dramatically increased through an acid-base neutralization reaction. This changes the compound into an ionic salt that is very water soluble and will distribute almost completely into the aqueous layer.

To illustrate how an acid-base extraction works, consider the extraction of a water-insoluble carboxylic acid (RCO_2H) from a toluene solution containing a mixture of neutral organic compounds. The carboxylic acid, although virtually insoluble in water, can be extracted from the toluene (organic) solution into the aqueous phase by extracting with a solution of sodium bicarbonate. The basic aqueous sodium bicarbonate solution will react with the carboxylic acid to give a water-soluble carboxylate salt.



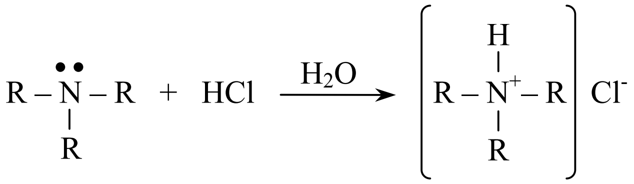
$$R-\overset{\overset{O}{||}}{C}-OH + NaHCO_3 \xrightarrow{H_2O} R-\overset{\overset{O}{||}}{C}-O^-Na^+ + CO_2 + H_2O$$

This salt will move into the aqueous solution, leaving the neutral organic compounds behind in the nonpolar toluene.

The carboxylic acid has been extracted from the organic layer, but now it is present in solution as the carboxylate salt. After the layers have been separated the carboxylic acid is regenerated using another acid-base reaction. Acidifying the basic solution with a mineral acid protonates the carboxylate ion, regenerating the carboxylic acid which has limited solubility in the aqueous solution. The isolated carboxylic acid product can then be recovered either by filtration or by extracting the carboxylic acid into fresh toluene and evaporating the solvent.

Carboxylic acids are strong enough acids (pK_a 3-5) to be neutralized to water-soluble salts by reaction with a weakly basic sodium bicarbonate solution. The much less acidic phenols (pK_a 8-10) will not react with sodium bicarbonate solution; phenols can be deprotonated to give water-soluble phenolate salts by extracting with an aqueous solution of a stronger base such as sodium hydroxide. The difference in the acidity of these two acidic functional groups allows them to be separated from each other in a mixture by using the proper alkaline solution in the acid-base extraction.

Organic amines, R_3N, are bases that can be removed from an organic solution by extracting them with aqueous acidic solutions to form water-soluble ammonium salts.



$$R-\underset{\underset{R}{|}}{\ddot{N}}-R \;+\; HCl \xrightarrow{H_2O} \left[R-\overset{\overset{H}{|}}{\underset{\underset{R}{|}}{N^{+}}}-R \right] Cl^{-}$$

Once the ammonium salt has been extracted into the aqueous phase and the organic and aqueous layers have been separated, the free amine can be regenerated from the ammonium ion by treating the aqueous solution with a base. This deprotonates the ammonium ion to give the less water-soluble free amine which can be collected either by filtration or by extracting the amine into fresh toluene and evaporating the solvent.

2.6.4 Separatory Funnel Technique

The choice of apparatus for an extraction is determined by the volumes of the solution being extracted and the extracting solutions. Typical extractions in the laboratory are done in a separatory funnel, while microscale extractions are done in a conical vial.

A separatory funnel is shown in the following figure 2-3. The funnel is fitted with a stopcock and a glass stopper. Make sure that the hole in the stopcock and the hole in the separatory funnel line up and that the stopcock fits snugly and turns smoothly without leaking. If the stopcock is made of glass, it should be lubricated with a small amount of stopcock grease so that it does not stick. Most newer stopcocks are made of Teflon® and need no grease. A small metal clip, rubber ring, or Teflon® nut with a washer and a ring at the end holds the stopcock in place. The stopper should also fit snugly. Avoid using stopcock grease on the stopper since the grease might dissolve in the organic solvent and contaminate the solution. For storage, remove the stopper and the stopcock, or wrap each with paper before inserting them into the funnel to prevent sticking.

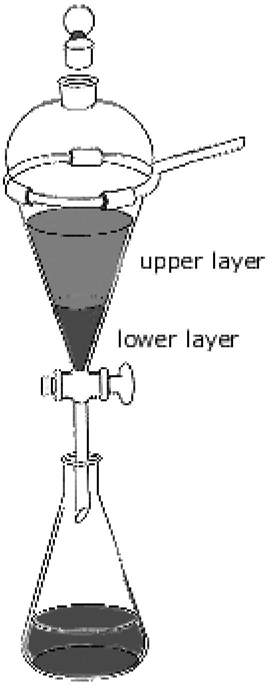


Figure 2-3 The Separation of System

A separatory funnel is top heavy, especially when nearly filled with liquid. Standing it upright in a beaker is a precarious situation at best. The separatory funnel should be supported in an iron ring of proper size attached to a ring stand. Before adding any liquid to theseparatory funnel, make sure that the stopcock is closed. One of the most common errors in extraction is pouring a liquid into the separatory funnel without first making sure that the stopcock is closed.

Add the two immiscible liquids for the extraction through a funnel into the separatory funnel, filling the separatory funnel only about three-fourths full to allow room for mixing. Place the stopper in the separatory funnel and, holding the stopper firmly in place with the index finger of one hand, remove the separatory funnel from the iron ring.

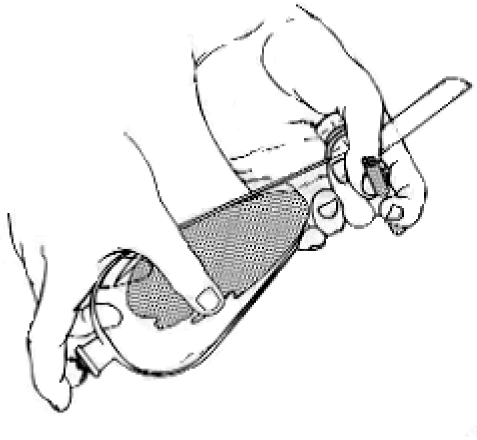


Figure 2-4 Shaking of Separatory Funnel

Invert the funnel, pointing the stem up away from the shaker (but not at someone else!), and carefully open the stopcock to vent any gases. A hissing sound may be heard as the gases are released through the stopcock. Close the stopcock and gently swirl the two liquids together to mix them. Vigorously shaking the contents is not only unnecessary but may prove deleterious by creating emulsions. It is common for pressure to build up in the separatory funnel during mixing, especially when using a volatile solvent such as ether or when neutralizing acids with carbonate or bicarbonate salts (that react with the acid to form CO_2 gas) so it is necessary periodically to stop mixing and open the stopcock to vent any pressure that has built up. After mixing is complete, close the stopcock and place the separatory funnel in the iron ring, remove the stopper and allow the layers to settle and separate; a clean interface should form between the two layers.

Place an Erlenmeyer flask or a beaker under the funnel, open the stopcock and drain the lower layer into the beaker or flask. As the interface between the two solvents approaches the stopcock, slow the rate of draining by adjusting the stopcock; then, remove all of the lower layer and retain all of the upper layer in the separatory funnel after draining.

If another extraction is going to be done on the **top** layer, leave it in the separatory funnel and add more of the next extracting solvent to the separatory funnel. If, however, another extraction is going to be done on the **lower** layer, pour the remaining upper layer out the top of the separatory funnel into a flask and then return the lower layer to the separatory funnel for the next extraction.

A common problem that may face in doing extractions is trying to determine which one of the two layers in the separatory funnel is the aqueous layer and which one is the organic layer. The heavier layer (i.e., the more dense liquid) is the lower layer, of course, but some organic liquids (e.g., benzene, diethyl ether, ethyl acetate) are lighter than water and some (e.g., chloroform, dichloromethane) are heavier than water, so, depending on the solvents being used, the organic phase might be the upper or the lower layer in the separatory funnel. The researcher could look up the densities of the two liquids to determine which is greater, but sometimes a high concentration of dissolved substances in the aqueous phase can cause it to be more dense than expected and to be found as the lower layer in the separatory funnel, even when extracting with an organic solvent with a density greater than water's. If unsure about which layer is which, carry out a simple test: mix a small sample of each layer with a few drops of water in a test tube and see if the two liquids are miscible; the aqueous solution will dissolve the water drops but the organic solution will be immiscible with the added water.

The Golden Rule of Extraction is: never throw a layer away until the end of the experiment, or until you are absolutely certain that you no longer need it. The most common mistake made during extraction is throwing the wrong layer down the drain or in the waste bottle, which means loss of material and starting the experiment over from the beginning.

2.6.5 Emulsions

The bugaboo of extractions is emulsions, foggy-looking mixtures containing tiny droplets of one liquid suspended in another that do not separate easily. If time permits, patience is the best solution; let the mixture stand until the emulsion breaks up and the two layers clearly separate. Sometimes adding salt or a saturated salt solution will help break up the emulsion, as will adding a little lighter or heavier solvent to the organic layer to increase the difference between the densities of the two layers. The best way to deal with emulsions is to avoid them. Gently swirling the contents of the separatory funnel during mixing instead of vigorously shaking them will help prevent emulsions from forming in the first place.

2.7 Chemistry of D2EHPA

D2EHPA or di-2-ethylhexyl phosphoric acid (C.A.S. 298-07-7) is one of organophosphoric acid derivative, well known as extractant commercially used for the extraction of the metal ion (23), which is an effective metal extractant, used for hydro-metallurgical recovery and separation of various metals like Zinc, Rare Earths, Cobalt, Nickel, etc (24). D2EHPA is chemical stable and relatively cheap (23). Principe et al reported that D2EHPA is stable even though vigorously agitates in 6N HCl for 31 days (25). The formula is $(C_8H_{17}O)_2P(O)OH$ with molecular weight of 322.431. Table 2-2 shows some physical properties of D2EHPA from MSDS.

Table 2-2 Some Physical Properties of D2EHPA (26)

Physical Properties		**Appearance**	**Remark**
Form		liquid	
Color		colorless	
Odor		slightly sweetish	
pH value at 22 g/l water		< 7	(20 ^{0}C)
Viscosity	dynamic	40 mPa*s	(20 ^{0}C)
Melting temperature		-50 ^{0}C	
Boiling temperature		not available	
Ignition temperature		> 300 ^{0}C	
Flash point		150 ^{0}C	
Explosion limits	lower	not available	
	upper	not available	
Vapour pressure		< 0.1 hPa	(20 ^{0}C)
Density		0.97 g/cm^3	(20 ^{0}C)
Solubility in	water	18 g/l	(20 ^{0}C)
	organic solvents	soluble	(20 ^{0}C)
Thermal decomposition		> 240 ^{0}C	

2.8 Solvent Extraction in Wastewater Treatment

Solvent extraction process using organophosphorus acid derivatives as extracting agents is potentially becoming an important recovery unit in hydrometallurgical and wastewater treatment process. Conventional solvent extraction processes are operated in devices such as packed towers, mixer-settlers, etc (27). There have been several reports in wastewater treatment using solvent extraction. Especially in using solvent extraction to recover some heavy metals. Cobalt and zinc recovery form copper sulphate solution by Solvent extraction was an example in application, which presented by Kongolo et al (28). The method mainly consisted of selective copper extraction with LIX 984, iron removal by precipitation with $CaCO_3$, simultaneous cobalt and zinc extraction with D2EHPA followed by their separation by selective stripping with sulfuric acid of different concentrations.

The efficiency of conventional solvent extraction process is subject to many factors, such as extraction time, concentration of extracting agent, temperature, etc. Many researchers discovered that extraction time and concentration of extraction agent can increased the extraction efficiency. Pandey et al investigated using di(2-ethylhexyl)phosphoric acid (D2EHPA), compared to Cyanex®272 in extraction of chromium (III) from spent tanning baths for chromium recovery (6). The results from solvent extraction using D2EHPA showed that when increasing extraction time from 30 seconds to 2 minutes, chromium extraction efficiencies using D2EHPA would increase from 90.0% to 95.0%, respectively. In the same way, when increasing D2EHPA dosage from 10% to 15%, chromium extraction efficiencies would increase from 85.2% to 95.0%, respectively. And they also investigated the stripping process using HCl acid to recover chromium. The results were similar to those for extraction; that is, the stripping efficiency increased from 65% to 80% when the stripping increased from 10 to 30 minutes, and the increasing of stripping efficiency from 35% to 80% when the HCl concentration increased from 1 M to 11 M.

Liquid-liquid extraction using phosphoric acid based extractant was applied to the extraction of nickel at macro-level concentration from sulphate/chloride solutions (7). The researcher studied effects from several factors, such as concentration of salt, concentration of extractant, and contact time. Most factors had positive effects to extraction efficiency. The increase of nickel extraction was found after increasing extractant concentration. And contact time only 1 minute was enough for reaching extraction equilibrium. In contrast, concentration of salt had adverse effect, i.e., Nickel extraction decreased with increasing sodium salt concentration.

There are other organophosphoric acid derivatives available for metal extraction. Cyanex®272 was used in solvent extraction of chromium using the pressure acid leaching technique (29), including the effects of various experimental variables such as metal oxidation state, pH, anions, extractant concentration, stripping contact time, and so forth. The results were the same as previously described, especially extractant concentration and stripping contact time, which were proportional to extraction efficiency.

Cyanex®923 is also one of extractants in the series of Cyanex® that is applied into solvent extraction of some heavy metals. There was investigation on the solvent extraction of titanium (IV) from acidic chloride solution (30). This research used Cyanex®923 in xylene as an extractant. The increasing of titanium (IV) extraction, with the total chloride concentration in the aqueous phase, as well as with the extraction concentration in the organic phase, were observed. The use of Cyanex® 923 for iron (III) extraction from acidic chloride solutions was also studied (31).This research used Cyanex®923 in xylene as an extractant as well. The results showed that the extraction efficiency increased with increasing concentration of both extractants and hydrochloric acid. The species extracted into the organic phase appeared to be $HFeCl_4$ with 2 mol of solvent. The other organophosphorus acid derivatives such as 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (EHEHPA) was also investigated on the extraction of titanium (IV) from acidic chloride solution. The organic phase consisted of EHEHPA as an extraction agent and xylene as a solvent (32). The increasing of extraction was observed after increasing extractant.

However, there are some metals that are difficult to be extracted by conventional extraction. (8) But the efficiency could be improved by conversion either aqueous phase or organic phase by functional chemical reaction during actual extraction. In the case of aqueous phase species, 1) a redox reaction of the metal ion, 2) a complexing reaction with water-soluble complexing agents, and 3) a complexing reaction with salting-out agents are all possible feasible solutions. While in the case of treatment in organic phase, three different reaction possibilities exist. These are 1) modification of the extractant or of the extracted species, 2) a synergistic effect obtained by adding extractants, and 3) a redox reaction for the extracted species.

Nishihama et al carried out a study on advanced liquid-liquid extraction systems for the separation of metal ions by a combination of conversion of the metal species with chemical reaction as described above (8). The results could be concluded that 1) metal ion in aqueous phase can be modified or converted by chemical reactions that can lead to selective extraction or stripping and thus, to high separation efficiencies, and 2) modification or conversion of the extracted species in the organic phase by an extra extractant (synergistic effect) and by redox reaction are a very feasible technique for improving the extraction and separation of metals.

The feasibility of using synergistic as an extracting agents was confirmed by Pandey et al who investigated the use of ammonia as synergistic extractant, and using di(2-ethylhexyl)phosphoric acid (D2EHPA) in extraction of chromium(III) from spent tanning baths for chromium recovery (6). The organic phases of their experiments were non-ammonated and 50%-ammonated D2EHPA in xylene with iso-decanol as the phase modifier. The relatively higher efficiency of chromium extraction was observed after adding ammonia solution for converting D2EHPA into ammonium salt.

TPEN (*N,N,N',N'*-tetrakis(2-pyridylmethyl)ethylenediamine) is one of synergistic extractant which was demonstrated by Takeshita (9). TPEN has strong affinity for Cd(II) and Zn(II), and converted into chelated form which is more soluble in organic phase. The stability constant for the formation of $Cd(TPEN)^{2+}$ and $Zn(TPEN)^{2+}$ were found to be greater than 10^{13}, indicating that complex of both metals were formed easily and very stable.

CHAPTER 3

MATERIALS AND METHODS

The solvent extraction technique using D2EHPA as an extracting agent was investigated in recovering of chromium. The true experimental research was conducted at the Laboratory of Sanitary Engineering Department, Faculty of Public Health, Mahidol University. Batch experiments were performed for this study.

3.1 Experimental Setup

3.1.1 Wastewater

The tannery wastewater used in this experiment was directly taken from the chrome tanning tank, in the chrome tanning process, from a tannery factory located in Samutprakarn Province, Thailand. A grab sample of wastewater obtained from the factory was used throughout the study.

3.1.2 Equipment

The equipments used in this experiment are listed below:

1) Shaker, speed 150 rpm
2) Separatory funnel, 250 ml
3) Glass apparatuses
4) pH meter
5) Hot plate
6) Hood
7) Glass microfibre filters (GF/C) paper No.42
8) Atomic Absorption Spectroscopy

3.1.3 Chemical Reagents

The chemical reagents used in this experiment are listed below:

1) Di-2-ethylhexylphosporic acid (D2EHPA), Fluka
2) 1-Decanol, Fluka
3) Ammonia solution 30%
4) Coconut oil, commercial grade
5) Sodium hydroxide
6) Hydrochloric acid
7) Nitric acid

3.2 Experimental Procedures

The chromium recovery experiment consists of 2 stages: extraction stage and recovery stage. The first extraction stage uses D2EHPA and NH_3 for extracting chromium (III) ions from tanning wastewater and transferring it into the organic phase. Three levels of three independent variables: NH_3 dosage (4%, 8%, 12% v/v of D2EHPA), D2EHPA dosage (10%, 20%, 30% v/v of organic phase), and extraction time (1, 3, 6 minute(s)) were investigated.

While the second stage, so called recovery stage, uses HCl acid for re-extracting chromium (III) ions from organic phase and transferring it back to the aqueous phase. Three levels of two independent variables: HCl concentration (3.6N, 4.8N, 6.0N) and recovery time (10, 30, 60 minutes) were investigated.

The profiles of both stages are illustrated in Figure 3-1. The overall procedures in this experimental are described below.

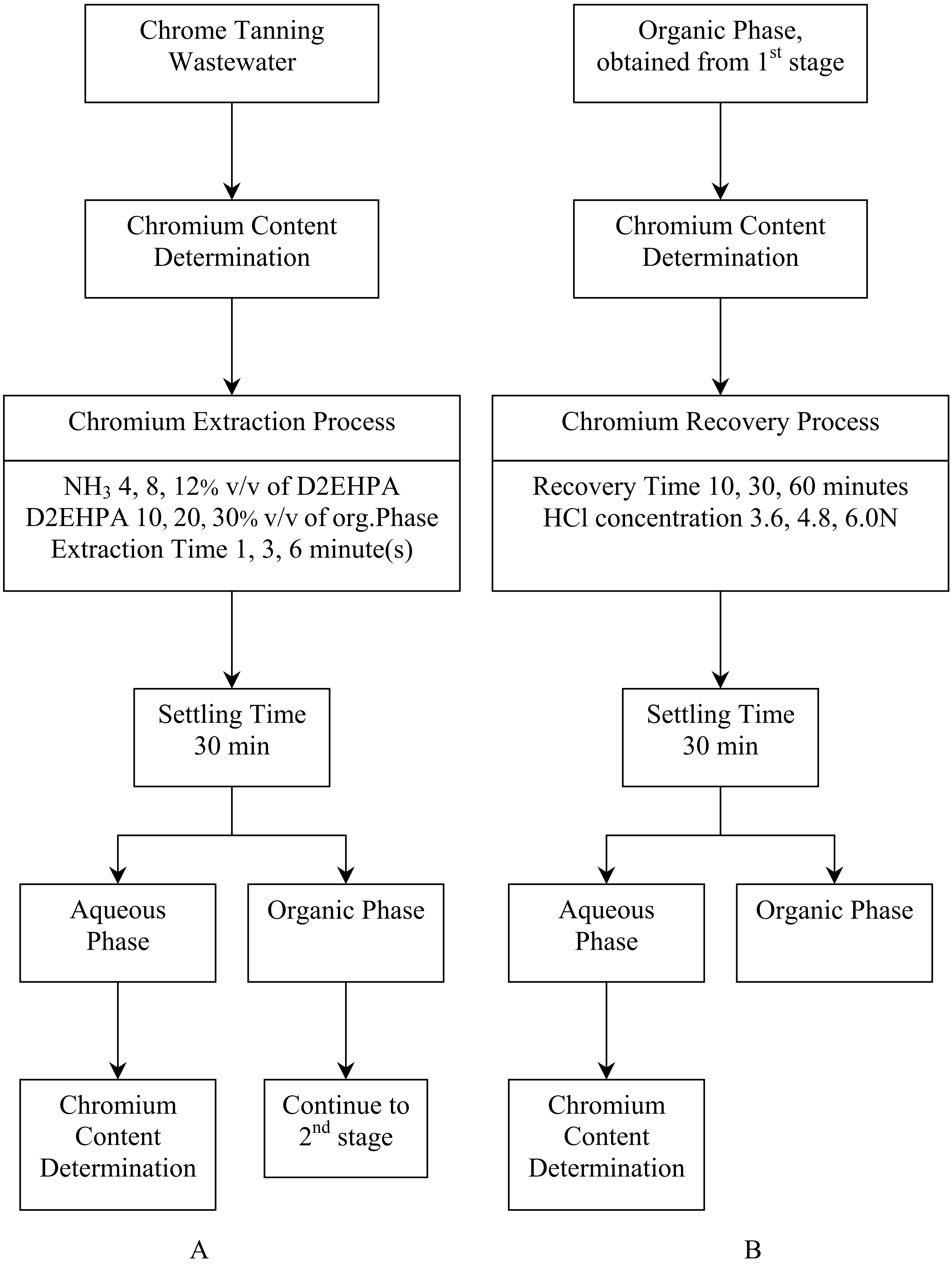


Figure 3-1 The Experimental Profile

A : Extraction Stage, B : Recovery Stage

3.2.1 Extraction Stage Procedures

The procedures in chromium extraction stage are described below:

1) Determine chromium content of tannery wastewater.
2) Adjust pH of wastewater to the range of 2 – 3.
3) Take 50.00 ml of wastewater from 2) into separatory funnel.
4) Prepare organic phase by
    - pipette D2EHPA dosage: 10%, 20%, 30% v/v of organic phase.
    - pipette 1-decanol 10% v/v of organic phase .
    - pipette NH_3 dosage: 4%, 8%, 12% v/v of D2EHPA.
    - add coconut oil to make final volume 50.00 ml.
5) Carefully pours organic phase from 4) into separatory funnel and close the cover tightly.
6) Shake the separatory funnel, using shaker at 150rpm for the extraction time: 1, 3, 6 minute(s).
7) Allow the separatory funnel to settle for 30 minutes. The emulsion will be separated into 2 layers:
    - upper layer is organic phase, which is further experimented onto the 2^{nd} stage.
    - lower layer is aqueous phase.
8) Determine the chromium content in the aqueous phase. Derive the chromium extraction efficiency.

3.2.2 Recovery Stage Procedures

The procedures in chromium recovery stage are described below:

1) Determine chromium content in organic phase from the 1st stage.

2) Prepare aqueous phase by

   - prepare HCl acid 3.6N, 4.8N, 6.0N.

3) Take 50.00 ml of prepared HCl acid from 2) into separatory funnel.

4) Slowly pour 50.00 ml of organic phase from 1st stage into separatory funnel. Close the cover tightly.

5) Shake the separatory funnel using shaker at 150rpm for the extraction time: 10, 30, 60 minutes.

6) Allow the separatory funnel to settle for 30 minutes. The emulsion will be separated into 2 layer.

   - upper layer is organic phase.
   - lower layer is aqueous phase.

7) Determine the chromium content in the aqueous phase. Derive the chromium recovery efficiency.

3.2.3 Analytical Method

All of chromium content determinations in this research followed the analytical method from the Standard Methods for Examination of Water and Wastewater, 21st Edition, 2000 (33). The atomic absorption spectroscopy was used to determine the contents of total Chromium. The concentration was expressed in term of ppm (part per million).

3.3 Statistical Analysis (34)

Three types of statistical analysis: mean comparison, correlation analysis, and regression analysis, were performed using SPSS for windows ver.12 (35), at 0.05 level of significance, to describe effects of independent variables on dependent variable in both stages.

The mean comparison implied the different between each average efficiency and the rest. In this process, when the data was normally distributed **and** their variances were homogenous, one-way ANOVA was used to compare the mean of the efficiency. When there were at least two levels of studied variable, which their efficiencies were significantly different, then, the Least Significant Difference's multiple comparison procedure was used to compare means of each pair group. In contrast, when the data was not normally distributed **or** their variances were not homogenous, Kruskal-Wallis H Test was used to compare the mean of the efficiency. When there were at least two levels of studied variable, which their efficiencies were significantly different, then, the Mann-Whitney U Test was used to compare means of each pair group.

Correlation analysis indicated the correlation between each independent variable and dependent variable. In this analysis, when the data was normally distributed, the correlation was determined in term of Pearson correlation coefficient. When the data was not normally distributed, the correlation was measured using Spearman correlation coefficient.

The final statistical analysis was regression analysis using stepwise method, which able to figure out the potential of each independent variable that had an effect on dependent variable. Moreover, stepwise regression was also able to predict the value of dependent variable from independent variables within studied range.

The overall statistical analysis procedures are concluded in Figure 3-2. The statistical hypotheses and interpretation of the results are summarized in Appendix B (Table B-1).

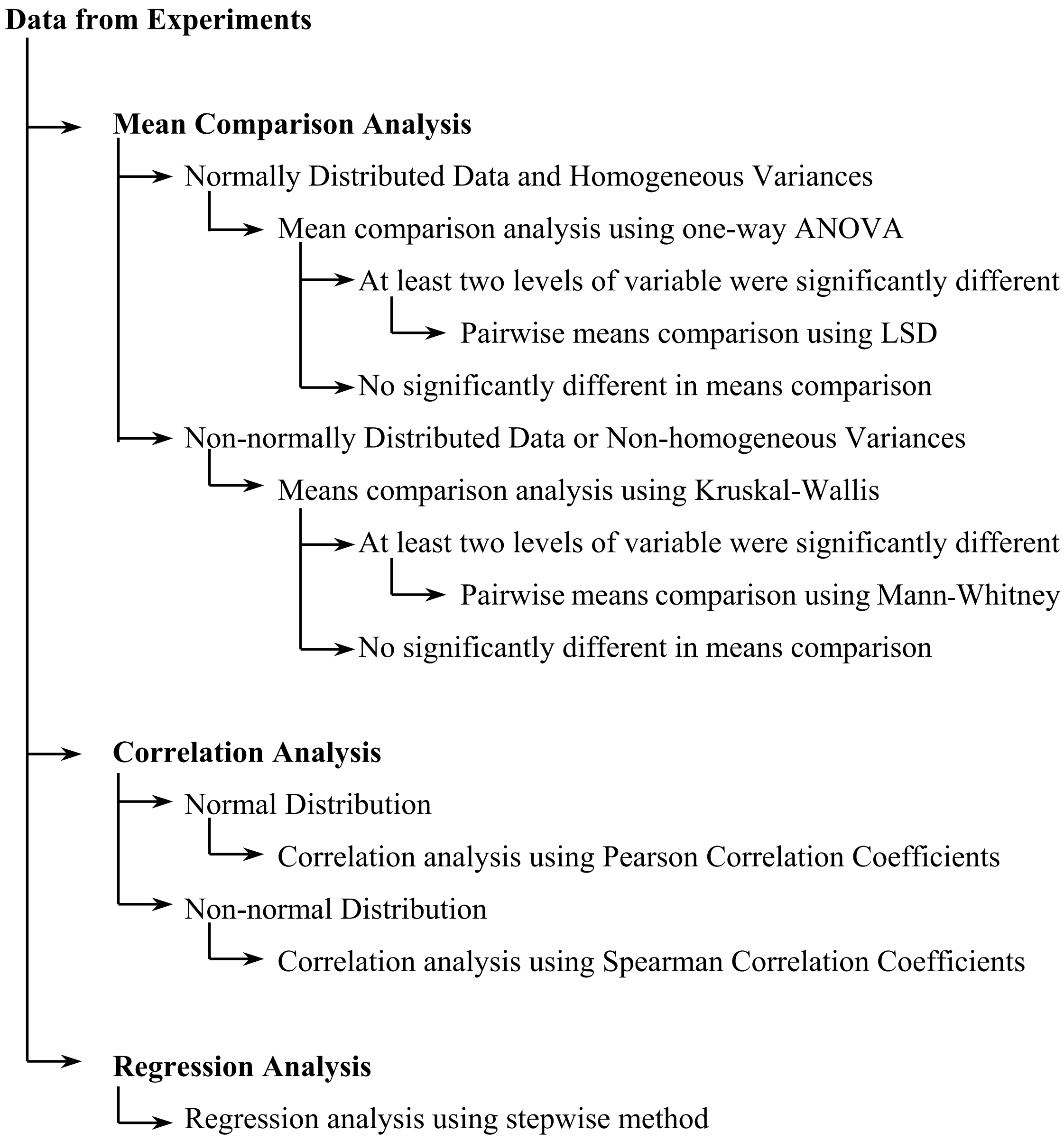


Figure 3-2 The Statistical Analysis Procedures

3.4 Experimental Design

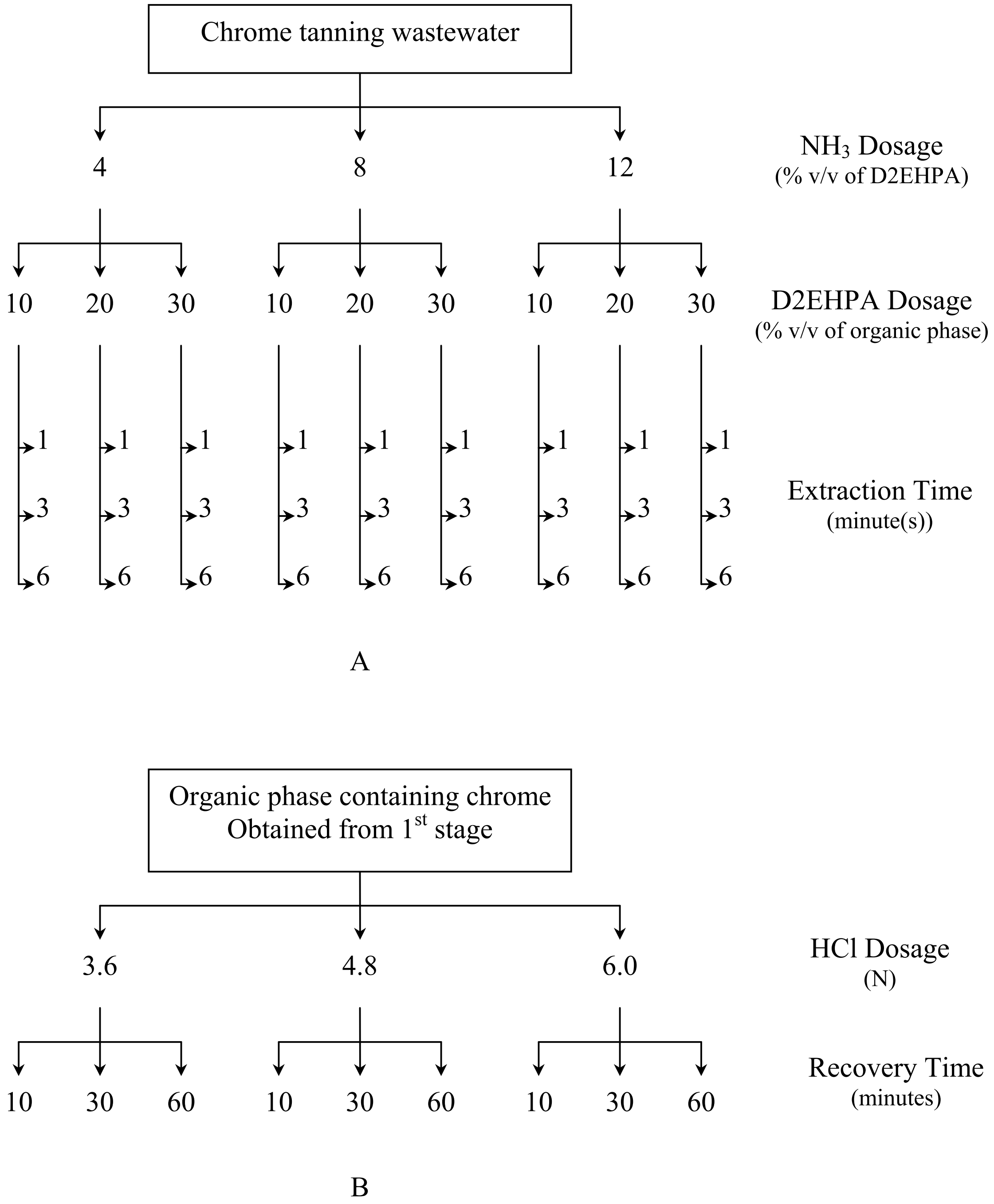


Figure 3-3 The Experimental Design (3 replicates)

A : Extraction Stage, B : Recovery Stage

CHAPTER 4

RESULTS

The experiment was divided into two stages; extraction stage and recovery stage. The results from both stages are presented as follows.

4.1 Tanning Wastewater Characteristics

The tannery wastewater used in this experiment was directly taken from the chrome tanning tank, in the chrome tanning process, from a tannery factory located in Samutprakarn Province, Thailand. The characteristics of tannery wastewater used in this study are presented in Table 4-1.

Table 4-1 Characteristics of Tanning Wastewater

Parameter	Unit	Values
pH		2.7
Suspend Solid	mg/l	97.2
COD	mg/l	4,250
Total Chromium	ppm	2,015.3

4.2 Chromium Extraction Efficiencies in Extraction Stage

In extraction stage, the effects of NH_3 dosage, D2EHPA dosage, and extraction time to chromium extraction efficiencies were investigated, and the results are described below.

4.2.1 Chromium Extraction Efficiencies at Different NH_3 Dosages

Three levels of NH_3 dosage (4%, 8%, 12% v/v of D2EHPA) were studied. These experiments were investigated with three levels of D2EHPA dosage (10%, 20%, 30% v/v of organic phase), and three levels of extraction time (1, 3, 6 minute(s)).

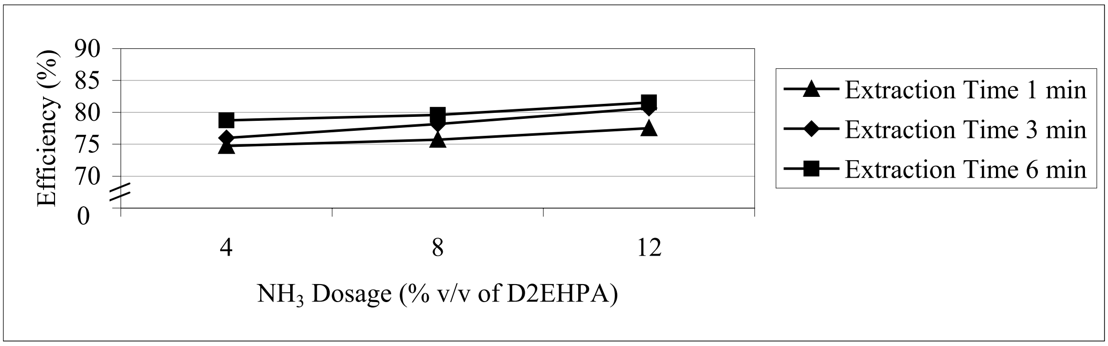
The first level of investigated NH_3 dosage was 4% v/v of D2EHPA. The desired amounts of D2EHPA for this research were 5ml, 10ml, and 15ml in 50ml of organic phase (10%, 20%, 30% v/v of organic phase, respectively), therefore this level of NH_3 required 0.2ml, 0.4ml, and 0.6ml of NH_3 (4% v/v of D2EHPA), respectively. The second level of NH_3 dosage was 8% v/v of D2EHPA, requiring 0.4ml, 0.8ml, 1.2ml of NH_3. While the last level of NH_3 was 12% v/v of D2EHPA, requiring 0.6ml, 1.2ml, 1.8ml of NH_3, respectively.

The increase of average chromium extraction efficiencies was achieved when the doses of NH_3 were increased. When compared the average chromium extraction efficiencies at different doses of NH_3, of any studied D2EHPA dosages and any studied extraction times, the results showed that the dose of NH_3 at 12% v/v of D2EHPA gave higher chromium extraction efficiency than those of 8% and 4%, respectively.

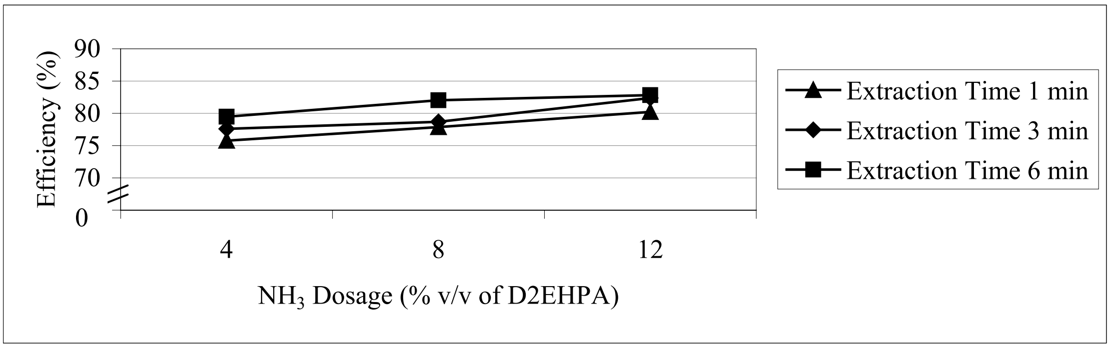
The average chromium extraction efficiencies at varied doses of NH_3 are shown in the Table 4-2. Figure 4-1 shows the graphic presentations of the different NH_3 dosages to average chromium extraction efficiencies.

Table 4-2 The Average Chromium Extraction Efficiencies at Different NH_3 Dosages

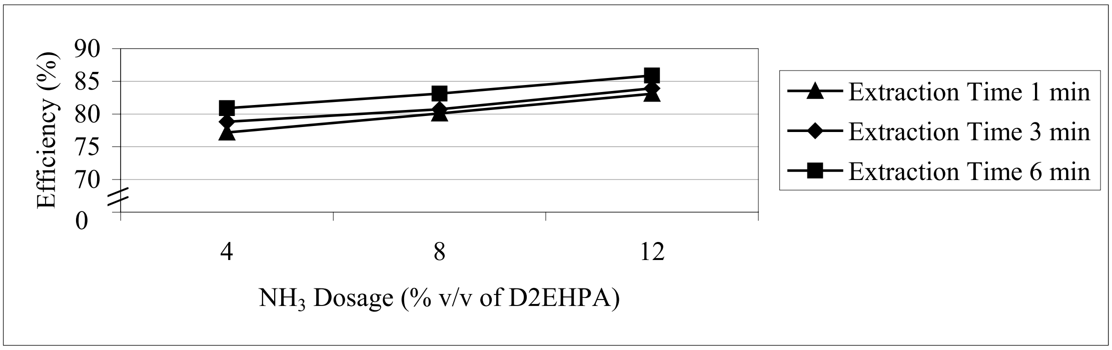
NH_3 Dosage (%v/v of D2EHPA)	D2EHPA Dosage (% v/v of Org. Phase)	Extraction Time (minute(s))	Chromium Extraction Efficiency (%)	
			Mean	SD
4	10	1	74.72	1.64
		3	75.97	1.75
		6	78.74	1.90
	20	1	75.77	1.11
		3	77.60	1.58
		6	79.48	1.68
	30	1	77.18	1.06
		3	78.83	0.89
		6	80.91	1.53
8	10	1	75.70	1.30
		3	78.17	1.74
		6	79.60	1.40
	20	1	77.88	1.70
		3	78.68	1.23
		6	82.02	2.23
	30	1	80.09	1.62
		3	80.73	1.50
		6	83.12	1.19
12	10	1	77.50	1.86
		3	80.21	2.10
		6	83.10	1.70
	20	1	80.67	1.85
		3	82.37	1.86
		6	83.92	1.36
	30	1	81.56	1.69
		3	82.82	1.38
		6	85.88	2.20



(a)



(b)



(c)

Figure 4-1 The Average Chromium Extraction Efficiencies Comparison at Different NH_3 Dosages, D2EHPA Dosages of (a) 10%, (b) 20%, (c) 30% v/v of organic phase, and Extraction Times of 1, 3, 6 minute(s)

4.2.2 Chromium Extraction Efficiencies at Different D2EHPA Dosages

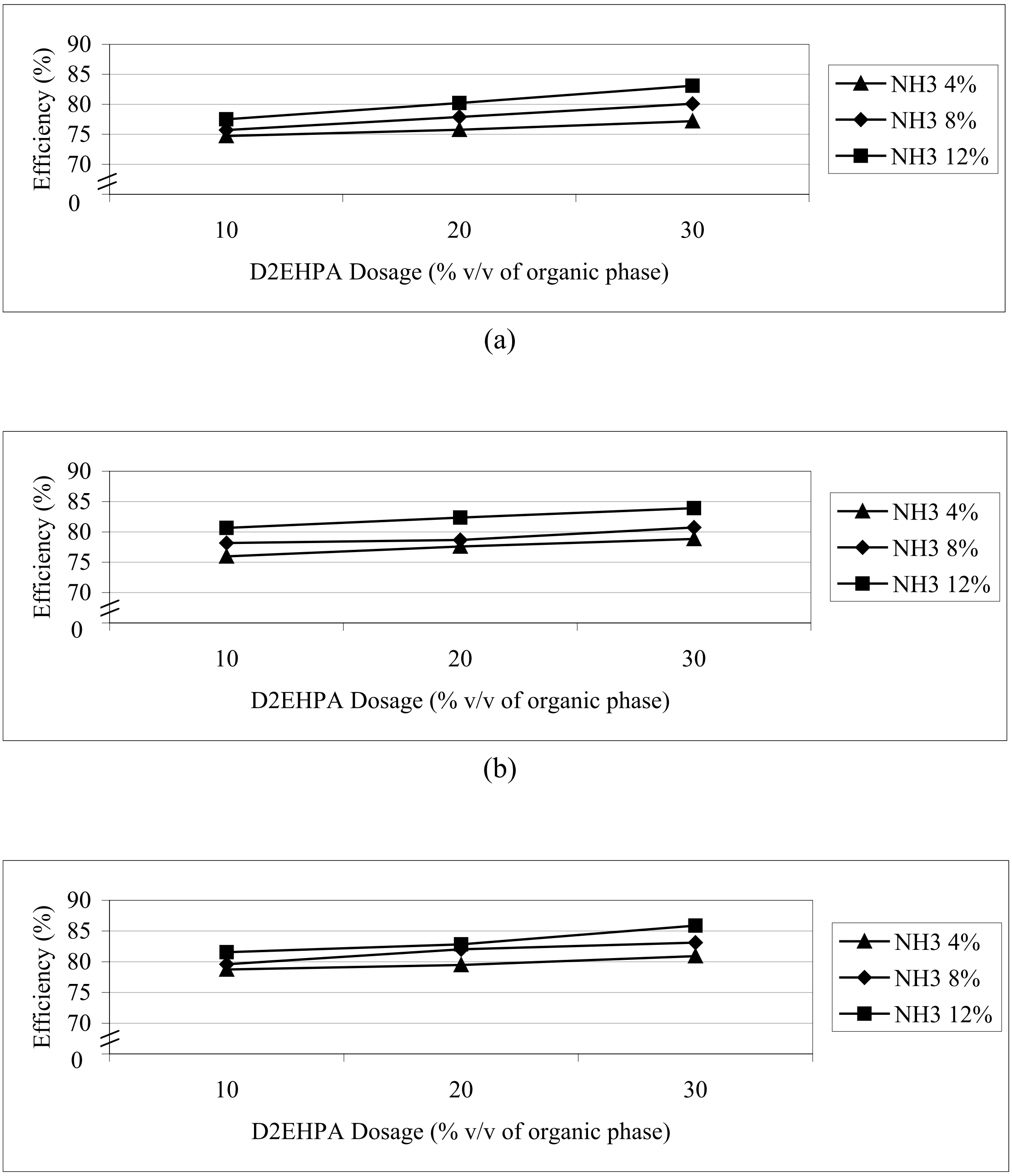
Three levels of D2EHPA dosage (10%, 20%, 30% v/v of organic phase) were studied. These experiments were investigated with three levels of extraction time (1, 3, 6 minute(s)), and three levels of NH_3 dosage (4%, 8%, 12% v/v of D2EHPA).

The results showed that average chromium extraction efficiencies were increased after increased D2EHPA dosages. When compared the average chromium extraction efficiencies at different doses of D2EHPA, of any studied extraction times and any studied NH_3 dosages, the results showed that the dose of D2EHPA at 30% v/v of organic phase gave higher chromium extraction efficiency than those of 20% and 10%, respectively.

The average chromium extraction efficiencies from all three investigated levels of D2EHPA dosage are shown in Table 4-3. The graphic presentations of the different D2EHPA dosages to average chromium extraction efficiencies are shown in figure 4-2.

Table 4-3 The Average Chromium Extraction Efficiencies at Different D2EHPA Dosages

D2EHPA Dosage (% v/v of Org. Phase)	Extraction Time (minute(s))	NH_3 Dosage (% v/v of DEHPA)	Chromium Extraction Efficiency (%)	
			Mean	SD
10	1	4	74.72	1.64
		8	75.70	1.30
		12	77.50	1.86
	3	4	75.97	1.75
		8	78.17	1.74
		12	80.67	1.85
	6	4	78.74	1.90
		8	79.60	1.40
		12	81.56	1.69
20	1	4	75.77	1.11
		8	77.88	1.70
		12	80.21	2.10
	3	4	77.60	1.58
		8	78.68	1.23
		12	82.37	1.86
	6	4	79.48	1.68
		8	82.02	2.23
		12	82.82	1.38
30	1	4	77.18	1.06
		8	80.09	1.62
		12	83.10	1.70
	3	4	78.83	0.89
		8	80.73	1.50
		12	83.92	1.36
	6	4	80.91	1.53
		8	83.12	1.19
		12	85.88	2.20



(a)

(b)

(c)

Figure 4-2 The Average Chromium Extraction Efficiencies Comparison at Different D2EHPA Dosages, Extraction Times of (a) 1, (b) 3, (c) 6 minute(s), and NH_3 Dosages of 4%, 8%, 12% v/v of D2EHPA

4.2.3 Chromium Extraction Efficiencies at Different Extraction Times

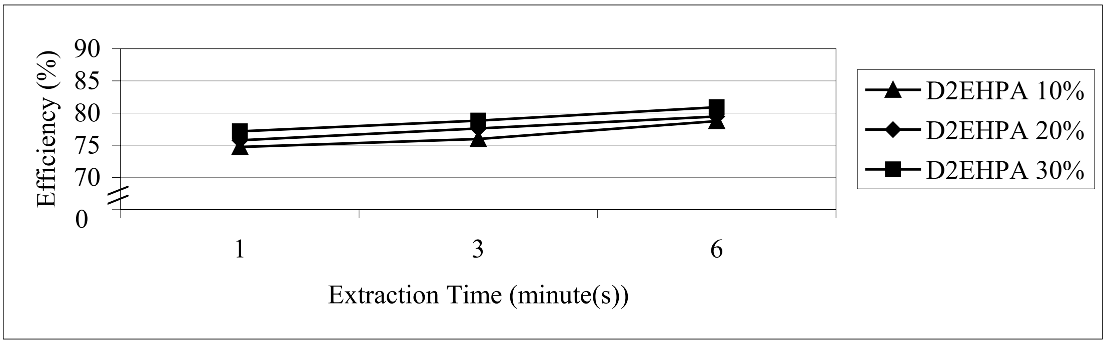
Three levels of extraction time (1, 3, 6 minute(s)) were studied. These experiments were investigated with three levels of NH_3 dosage (4%, 8%, 12% v/v of D2EHPA), and three levels of D2EHPA dosage (10%, 20%, 30% v/v of organic phase).

The results showed that average chromium extraction efficiencies were increased while the extraction times increased. When compared the average chromium extraction efficiencies at different extraction times, of any studied NH_3 dosages and any studied D2EHPA dosages, the results showed that the extraction time at 6 minutes gave higher chromium extraction efficiency than those of 3 minutes and 1 minute, respectively.

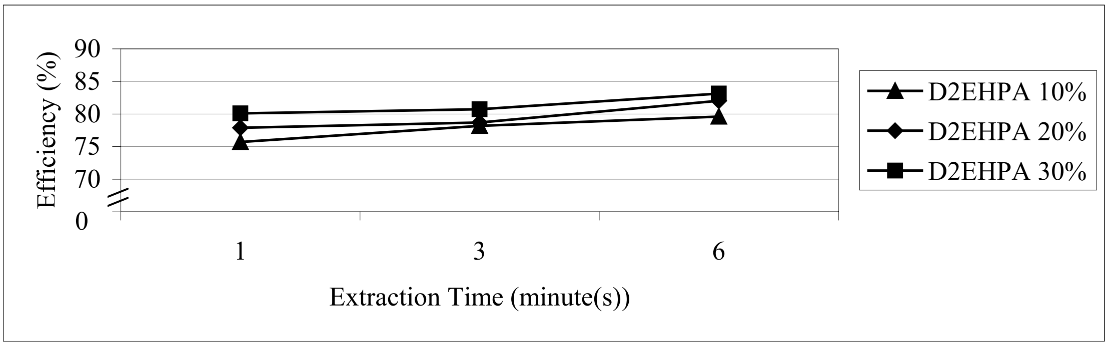
The overall average chromium extraction efficiencies from three investigated levels of extraction time are shown in Table 4-4. Figure 4-3 presents the comparisons of average chromium extraction efficiencies by different extraction times, NH_3 dosages, and D2EHPA dosages.

Table 4-4 The Average Chromium Extraction Efficiencies at Different Extraction Times

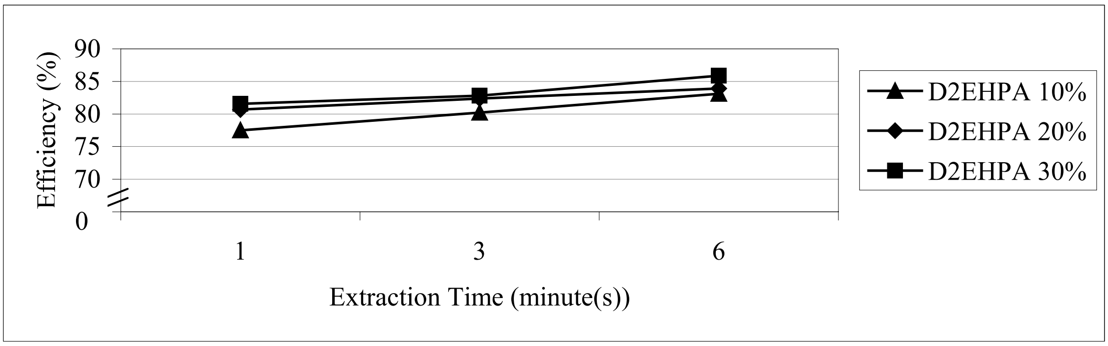
Extraction Time (minute(s))	NH_3 Dosage (% v/v of DEHPA)	D2EHPA Dosage (% v/v of Org Phase)	Chromium Extraction Efficiency (%)	
			Mean	SD
1	4	10	74.72	1.64
		20	75.77	1.11
		30	77.18	1.06
	8	10	75.70	1.30
		20	77.88	1.70
		30	80.09	1.62
	12	10	77.50	1.86
		20	80.21	2.10
		30	83.10	1.70
3	4	10	75.97	1.75
		20	77.60	1.58
		30	78.83	0.89
	8	10	78.17	1.74
		20	78.68	1.23
		30	80.73	1.50
	12	10	80.67	1.85
		20	82.37	1.86
		30	83.92	1.36
6	4	10	78.74	1.90
		20	79.48	1.68
		30	80.91	1.53
	8	10	79.60	1.40
		20	82.02	2.23
		30	83.12	1.19
	12	10	81.56	1.69
		20	82.82	1.38
		30	85.88	2.20



(a)



(b)



(c)

Figure 4-3 The Average Chromium Extraction Efficiencies Comparison at Different Extraction Times, NH_3 Dosages of (a) 4%, (b) 8%, (c) 12% v/v of D2EHPA, and D2EHPA Dosages of 10%, 20%, 30% v/v of organic phase

4.3 Chromium Recovery Efficiencies in Recovery Stage

In recovery stage, the effects of HCl concentration and recovery time to chromium recovery efficiencies were investigated, as the results are shown below.

4.3.1 Chromium Recovery Efficiencies at Different HCl Concentrations

Three levels of HCl concentration (3.6N, 4.8N, 6.0N) were investigated with three levels of recovery time (10, 30, 60 minutes).

The results showed that when increased the concentration of HCl acid, the average chromium recovery efficiencies were also increased. When compared the average chromium recovery efficiencies at different HCl concentrations, of any studied recovery times, the results showed that the average chromium recovery efficiency at 6.0N HCl was higher than those of the 4.8N and 3.6N, respectively.

The overall average chromium recovery efficiencies from the three investigated levels of HCl concentration are shown in Table 4-5. The graphic presentations of average chromium recovery efficiencies, with varied HCl concentrations, are shown in Figure 4-4.

Table 4-5 The Average Chromium Recovery Efficiencies at Different HCl Concentrations

HCl Concentration (N)	Recovery Time (minutes)	Chromium Recovery Efficiencies (%)	
		Mean	SD
3.6	10	22.78	1.27
	30	43.33	1.32
	60	47.63	1.01
4.8	10	31.49	1.52
	30	57.17	1.80
	60	58.46	1.08
6.0	10	35.24	1.95
	30	67.76	1.66
	60	67.33	2.00

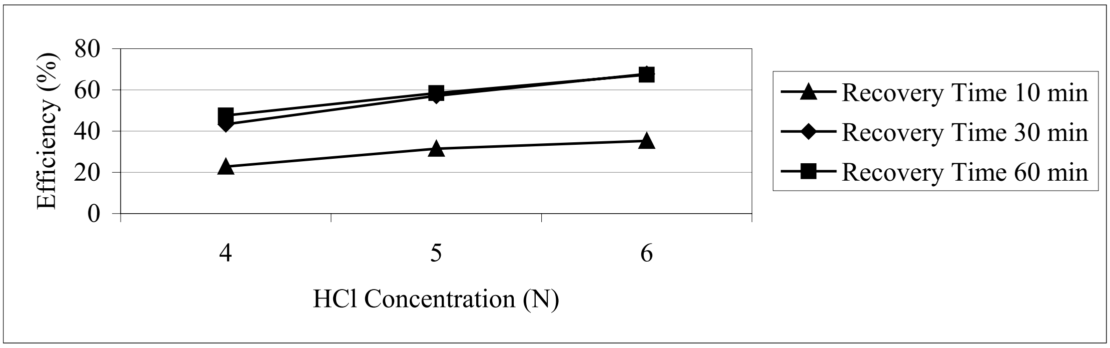


Figure 4-4 The Average Chromium Recovery Efficiencies Comparison at Different HCl Concentrations, Recovery Times of 10, 30, 60 minutes

4.3.2 Chromium Recovery Efficiencies at Different Recovery Times

Three levels of recovery time (10, 30, 60 minutes) were investigated with three levels of HCl concentration (3.6N, 4.8N, 6.0N).

The results showed that chromium recovery efficiencies were increased when the recovery times increased. When compared the average chromium recovery efficiencies at different recovery times, of any studied HCl concentrations, the results showed that the recovery time at 60 minutes gave higher chromium recovery efficiency than those of 30 minutes and 10 minutes, respectively.

The overall average chromium recovery efficiencies from three investigated levels of recovery time are shown in Table 4-6. Figure 4-5 shows the graphic presentations of the different recovery times to average chromium recovery efficiencies.

Table 4-6 The Average Chromium Recovery Efficiencies at Different Recovery Times

Recovery Time	HCl Concentration	Chromium Recovery Efficiencies (%)	
(minutes)	(N)	Mean	SD
10	3.6	22.78	1.27
	4.8	31.49	1.52
	6.0	35.24	1.95
30	3.6	43.33	1.32
	4.8	57.17	1.80
	6.0	67.76	1.66
60	3.6	47.63	1.01
	4.8	58.46	1.08
	6.0	67.33	2.00

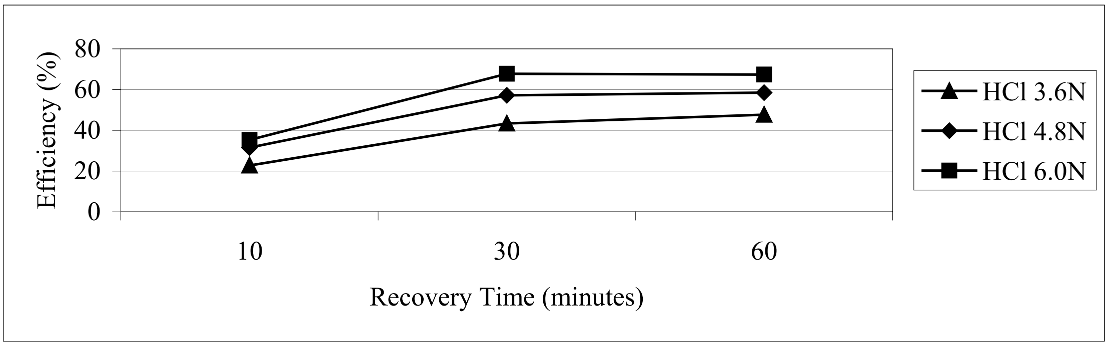


Figure 4-5 The Average Chromium Recovery Efficiencies Comparison at Different Recovery Times, HCl Concentrations of 3.6N, 4.8N, 6.0N

4.4 Statistical Analysis in Extraction Stage

In extraction stage, three independent variables were NH_3 dosage, D2EHPA dosage, and extraction time, while dependent variable was chromium extraction efficiency. The results of mean comparison, correlation analysis, and regression analysis are shown as follow.

4.4.1 The Mean Comparison of Chromium Extraction Efficiency

The results of mean comparison of chromium extraction efficiency at different levels of independent variables (NH_3 dosage, D2EHPA dosage, and extraction time), evaluated by appropriate statistical technique following the statistical analysis procedures in chapter 3, are shown below.

4.4.1.1 Mean Comparison at Different NH_3 Dosages

The test of normality, which presented in Appendix B (Table B-2), showed that average chromium extraction efficiencies at different NH_3 dosages were normally distributed (P-value = 0.200 for all doses of NH_3). And the test of homogeneity of variance, which presented in Appendix B (Table B-3), showed that the variances of average chromium extraction efficiencies at different NH_3 dosages were homogenous (P-value = 0.741).

The results from test of normality and test of homogeneity of variances indicated that one-way ANOVA analysis could be applied to the mean comparison at studied NH_3 dosages. The one-way ANOVA analysis, which presented in Appendix B (Table B-4), showed that there were at least two levels of NH_3 dosage yielded average chromium extraction efficiencies significantly different (P-value < 0.001).

Then LSD's multiple comparison was used to compare each pair of average chromium extraction efficiencies at studied levels of NH_3 dosage. The LSD's multiple comparison, which presented in Appendix B (Table B-5), showed that the average chromium extraction efficiency at NH_3 dose of 4% v/v of D2EHPA was significantly different from those of 8% and 12%, respectively (P-value $\leq$ 0.05). The results of mean comparison are concluded in Table 4-7.

Table 4-7 The Mean Comparison of Chromium Extraction Efficiencies at Different NH_3 Dosages

Independent Variable	Value (% v/v of D2EHPA)	Efficiency (%)		ANOVA			LSD	
		Mean	SD	df	F-test	P-value	Mean Different	P-value
	4	77.69	2.28				4% ≠ 8%	0.008
NH_3 Dosage	8	79.56	2.54	2, 78	19.752	< 0.001	8% ≠ 12%	0.001
	12	82.00	2.75				4% ≠ 12%	< 0.001

4.4.1.2 Mean Comparison at Different D2EHPA Dosages

The test of normality, which presented in Appendix B (Table B-6), showed that average chromium extraction efficiencies at different D2EHPA dosages were normally distributed (P-value = 0.200 for all doses of D2EHPA). And the test of homogeneity of variance, which presented in Appendix B (Table B-7), showed that the variances of average chromium extraction efficiencies at different D2EHPA dosages were homogenous (P-value = 0.906).

The results from test of normality and test of homogeneity of variances indicated that one-way ANOVA analysis could be applied to the mean comparison at studied D2EHPA dosages. The one-way ANOVA analysis, which presented in Appendix B (Table B-8), showed that there were at least two levels of D2EHPA dosage yielded average chromium extraction efficiencies significantly different (P-value < 0.001).

Then LSD's multiple comparison was used to compare each pair of average chromium extraction efficiencies at studied levels of D2EHPA dosage. The LSD's multiple comparison, which presented in Appendix B (Table B-9), showed that the average chromium extraction efficiency at D2EHPA dose of 10% v/v of organic phase was significantly different from those of 20% and 30%, respectively ($P\text{-value} \leq 0.05$). The results of mean comparison are concluded in Table 4-8.

Table 4-8 The Mean Comparison of Chromium Extraction Efficiencies at Different D2EHPA Dosages

Independent Variable	**Value**	**Efficiency (%)**		**ANOVA**			**LSD**	
	(% v/v of Org.Phase)	**Mean**	**SD**	**df**	**F-test**	**P-value**	**Mean Different**	**P-value**
D2EHPA Dosage	10	78.07	2.64	2, 78	10.690	< 0.001	10% ≠ 20%	0.039
	20	79.65	2.72				20% ≠ 30%	0.014
	30	81.53	2.89				10% ≠ 30%	< 0.001

4.4.1.3 Mean Comparison at Different Extraction Times

The test of normality, which presented in Appendix B (Table B-10), showed that average chromium extraction efficiencies at different extraction times were normally distributed (P-value = 0.200 for all extraction times). And the test of homogeneity of variance, which presented in Appendix B (Table B-11), showed that the variances of average chromium extraction efficiencies at different extraction times were homogenous (P-value = 0.782).

The results from test of normality and test of homogeneity of variances indicated that one-way ANOVA analysis could be applied to the mean comparison at studied extraction times. The one-way ANOVA analysis, which presented in Appendix B (Table B-12), showed that there were at least two levels of extraction time yielded average chromium extraction efficiencies significantly different (P-value < 0.001).

Then LSD's multiple comparison was used to compare each pair of average chromium extraction efficiencies at studied levels of extraction times. The LSD's multiple comparison, which presented in Appendix B (Table B-13), showed that the average chromium extraction efficiency at extraction time of 1 minute was significantly different from those of 3 minutes and 6 minutes, respectively (P-value $\leq$ 0.05). The results of mean comparison are concluded in Table 4-9.

Table 4-9 The Mean Comparison of Chromium Extraction Efficiencies at Different Extraction Times

Independent Variable	**Value** (minute(s))	**Efficiency (%)**		**ANOVA**			**LSD**	
		Mean	**SD**	**df**	**F-test**	**P-value**	**Mean Different**	**P-value**
Extraction Time	1	78.02	2.89	2, 78	11.466	< 0.001	$1_{min} \neq 3_{min}$	0.030
	3	79.66	2.72				$3_{min} \neq 6_{min}$	0.012
	6	81.57	2.57				$1_{min} \neq 6_{min}$	< 0.001

4.4.2 The Correlation Analysis of Chromium Extraction Efficiency

The results of correlation analysis of chromium extraction efficiency with each independent variable (NH_3 dosage, D2EHPA dosage, and extraction time), evaluated by appropriate statistical technique following the statistical analysis procedures in chapter 3, are shown below.

4.4.2.1 Correlation of Extraction Efficiency and NH_3 Dosage

The test of normality, which presented in Appendix B (Table B-2), showed that average chromium extraction efficiencies at different NH_3 dosages were normally distributed. Which indicated that Pearson correlation analysis could be applied to determine the correlation between chromium extraction efficiency and NH_3 dosage. The Pearson correlation analysis, which presented in Appendix B (Table B-14), showed that NH_3 dosage was significantly correlated with chromium extraction efficiency (P-value < 0.001). The results also indicated that NH_3 dosage caused positively effect to chromium extraction efficiency (Pearson correlation coefficient = 0.578).

4.4.2.2 Correlation of Extraction Efficiency and D2EHPA Dosage

The test of normality, which presented in Appendix B (Table B-6), showed that average chromium extraction efficiencies at different D2EHPA dosages were normally distributed. Which indicated that Pearson correlation analysis could be applied to determine the correlation between chromium extraction efficiency and D2EHPA dosage. The Pearson correlation analysis, which presented in Appendix B (Table B-15), showed that D2EHPA dosage was significantly correlated with chromium extraction efficiency (P-value < 0.001). The results also indicated that D2EHPA dosage had positively effect to chromium extraction efficiency (Pearson correlation coefficient = 0.463).

4.4.2.3 Correlation of Extraction Efficiency and Extraction Time

The test of normality, which presented in Appendix B (Table B-10), showed that average chromium extraction efficiencies at different extraction times were normally distributed. Which indicated that Pearson correlation analysis could be applied to determine the correlation between chromium extraction efficiency and extraction time. The Pearson correlation analysis, which presented in Appendix B (Table B-16), showed that extraction time was significantly correlated with chromium extraction efficiency (P-value < 0.001). The results also indicated that extraction time had positively effect to chromium extraction efficiency (Pearson correlation coefficient = 0.475).

4.4.3 The Regression of Independent Variables in Extraction Stage

The model summary from stepwise multiple regression analysis is presented in Appendix B (Table B-17). The results showed that all three independent variables (NH_3 dosage, extraction time, and D2EHPA dosage) had effects on dependent variable (chromium extraction efficiency) of 32.6%, 22.3%, and 21.7%, respectively. These results also implied that NH_3 dosage had the greatest effect on chromium extraction efficiency, than extraction time and D2EHPA dosage, respectively.

Moreover, stepwise multiple regression analysis, which presented in Appendix B (Table B-18) was also indicated that, within studied range, all three independent variables (NH_3 dosage, D2EHPA dosage, and extraction time) were able to apply (P-value < 0.001) into the equation for predicting the dependent variable (chromium extraction efficiency), as shown below;

$$Y = 69.625 + 0.539X_1 + 0.173X_2 + 0.705X_3$$

where; Y = chromium extraction efficiency
X_1 = NH_3 dosage; 4 - 12% v/v of D2EHPA
X_2 = D2EHPA dosage; 10 - 30 % v/v of organic phase
X_3 = extraction time; 1 – 6 minute(s)

4.5 Statistical Analysis in Recovery Stage

In recovery stage, two independent variables were HCl concentration and recovery time, while dependent variable was chromium recovery efficiency. The results of mean comparison, correlation analysis, and regression analysis are shown as follow.

4.5.1 The Mean Comparison of Chromium Recovery Efficiency

The results of mean comparison of chromium recovery efficiency at different levels of independent variables (HCl concentration and recovery time), evaluated by appropriate statistical technique following the statistical analysis procedures in chapter 3, are shown below.

4.5.1.1 Mean Comparison at Different HCl Concentrations

The test of normality, which presented in Appendix B (Table B-19), showed that average chromium recovery efficiencies at different HCl concentrations were not normally distributed ($P\text{-value} \leq 0.05$ for all HCl concentrations). And the tests of homogeneity of variance, which presented in Appendix B (Table B-20), showed that the variances of average chromium recovery efficiencies at different HCl concentrations were homogenous ($P\text{-value} = 0.195$).

The results from test of normality and test of homogeneity of variances indicated that Kruskal-Wallis H Test could be applied to the mean comparison at studied HCl concentrations. The Kruskal-Wallis H Test, which presented in Appendix B (Table B-21), showed that there were at least two levels of HCl concentrations yielded average chromium recovery efficiencies significantly different (P-value = 0.028).

Then Mann-Whitney U Test was used to compare each pair of average chromium recovery efficiencies at studied levels of HCl concentration. The Mann-Whitney U Test, which presented in Appendix B (Table B-22 to Table B-24), showed that the average chromium recovery efficiency at HCl concentration of 3.6N was significantly different from those of 4.8N and 6.0N, respectively (P-value ≤ 0.05). The results of mean comparison are concluded in Table 4-10.

Table 4-10 The Mean Comparison of Chromium Recovery Efficiency at Different HCl Concentrations

Independent Variable	**Value**	**Efficiency (%)**		**Kruskal-Wallis H test**			**Mann-Whitney U test**	
	(N)	**Mean**	**SD**	**df**	χ^2	**P-value**	**Mean Different**	**P-value**
HCl concentration	3.6	37.91	11.55	2	7.143	0.028	3.6N≠ 4.8N	0.47
	4.8	49.04	13.24				4.8N≠ 6.0N	0.47
	6.0	56.78	16.23				3.6N≠ 6.0N	0.47

4.5.1.2 Mean Comparison at Different Recovery Times

The test of normality, which presented in Appendix B (Table B-25), showed that average chromium recovery efficiencies at different recovery times were normally distributed (P-value = 0.200 for all recovery times). And the test of homogeneity of variance, which presented in Appendix B (Table B-26), showed that the variances of average chromium recovery efficiencies at different recovery times were homogenous (P-value = 0.782).

The results from test of normality and test of homogeneity of variances indicated that one-way ANOVA analysis could be applied to the mean comparison at studied recovery times. The one-way ANOVA analysis, which presented in Appendix B (Table B-27), showed that there were at least two levels of recovery time yielded average chromium recovery efficiencies significantly different (P-value < 0.001).

Then LSD's multiple comparison was used to compare each pair of average chromium recovery efficiencies at studied levels of recovery time. The LSD's multiple comparison, which presented in Appendix B (Table B-28), showed that the average chromium recovery efficiency at recovery time of 10 minutes was significantly different from those of 30 minutes and 60 minutes (P-value $\leq$ 0.05). However, there was no significantly different between recovery time of 30 minutes and 60 minutes (P-value = 0.675). The results of mean comparison are concluded in Table 4-11.

Table 4-11 The Mean Comparison of Chromium Recovery Efficiencies at Different Recovery Times

Independent Variable	Value (minutes)	Efficiency (%)		ANOVA			LSD	
		Mean	SD	df	F-test	P-value	Mean Different	P -value
Recovery Time	10	29.84	5.71	2, 24	29.927	< 0.001	$10_{min} \neq 30_{min}$	< 0.001
	30	56.09	10.70				$10_{min} \neq 60_{min}$	< 0.001
	60	57.81	8.64				$30_{min} = 60_{min}$	0.675

4.5.2 The Correlation Analysis of Chromium Recovery Efficiency

The results of correlation analysis of chromium recovery efficiency with each independent variable (HCl concentration and recovery time), evaluated by appropriate statistical technique following the statistical analysis procedures in chapter 3, are shown below.

4.5.2.1 Correlation of Recovery Efficiency and HCl Concentration

The test of normality, which presented in Appendix B (Table B-19), showed that average chromium recovery efficiencies at different HCl Concentrations were non-normally distributed. Which indicated that Spearman correlation analysis could be applied to determine the correlation between chromium recovery efficiency and HCl Concentration. The Spearman correlation analysis, which presented in Appendix B (Table B-29), showed that HCl Concentration was significantly correlated with chromium recovery efficiency (P-value = 0.005). The results also indicated that recovery time had positively effect to chromium recovery efficiency. (Spearman correlation coefficient = 0.524)

4.5.2.2 Correlation of Recovery Efficiency and Recovery Time

The test of normality, which presented in Appendix B (Table B-25), showed that, average chromium recovery efficiencies at different recovery times were normally distributed. Which indicated that Pearson correlation analysis could be applied to determine the correlation of chromium recovery efficiency and recovery time. The Pearson correlation analysis, which presented in Appendix B (Table B-30), showed that recovery time was significantly correlated with average chromium recovery efficiency (P-value < 0.001). The results also indicated that recovery time had positively effect to chromium recovery efficiency (Pearson correlation coefficient = 0.705).

4.5.3 The Regression of Independent Variable in Recovery Stage

The model summary from stepwise multiple regression analysis is presented in Appendix B (Table B-31). The results showed that all two independent variables (recovery time and HCl concentration) had effect to dependent variable (chromium recovery efficiency) of 47.7% and 25.8%, respectively. These results also implied that recovery time had greater effect on chromium recovery efficiency than HCl concentration.

Moreover, stepwise multiple regression analysis, which presented in Appendix B (Table B-32), was also indicated that, within studied range, all two independent variables (HCl concentration and recovery time) were able to apply (P-value < 0.001) into the equation for predicting the dependent variable (chromium recovery efficiency), as shown below;

$$Y = (-7.148) + 7.681X_1 + 0.520X_2$$

where; Y = chromium recovery efficiency
X_1 = HCl concentration, 3.6 – 6.0 N
X_2 = recovery time; 10 – 60 minutes

4.6 The Best Level of Each Variable

After both stages were investigated with respect to chromium recovery, the best statistical condition of each stage could be figured out from the results.

4.6.1 The Best Level in Extraction Stage

Extraction time of 6 minutes, D2EHPA dosage of 30% v/v of organic phase, and NH_3 dosage of 12% v/v of D2EHPA were found to be the best statistical condition of investigated levels in extraction stage, which yielded average chromium extraction efficiency of 85.88% (SD = 2.20%).

4.6.2 The Best Level in Recovery Stage

Recovery time of 30 minutes with 6N HCl were the best statistical condition of investigated levels in recovery stage, which yielded average chromium recovery efficiency of 67.76% (SD = 1.66%).

CHAPTER 5

DISCUSSION

The study of chromium recovery from tanning wastewater using the solvent extraction technique, consisted of two stages; extraction stage and recovery stage. Research results were already investigated in the previous chapter. In this chapter, the effects to the efficiency of all experimental variables for both stages are delineated below.

5.1 The Effect of Variables in Extraction Stage

There were three investigated variables in the extraction stage, NH_3 dosage, D2EHPA dosage, and extraction time. The effect of each variable is described as follows.

5.1.1 The Effect of NH_3 Dosage

The investigation on NH_3 dosage was exercised in three levels: 4%, 8%, and 12% v/v of D2EHPA. The average chromium extraction efficiencies of 77.69%, 79.56%, and 82.00% of were achieved for the NH_3 dosage of 4%, 8%, and 12% v/v of D2EHPA, respectively. The statistical analysis showed that the average chromium extraction efficiency at NH_3 dosage 12% v/v of D2EHPA was significantly different from those of 8% and 4%, respectively.

In extraction stage, NH_3 dosage had dominant effect to chromium extraction efficiency, and corresponded to the first hypothesis of extraction stage, which stated that, NH_3 dosage 12% v/v of D2EHPA would give higher average chromium extraction efficiency than those of 8% and 4%.

NH_3 was used to increase the pH of the organic phase, as demon-strated by Pandy et al (6). In their study, D2EHPA ammonated at 50% was performed to increase the efficiency of chromium extraction. Moreover, NH_3 was also a synergistic extracting agent, which similar to the research by Takeshita et al (9). They investigated the use of TPEN in synergistic extraction system. They found that metals extraction efficiency would be increased when nitrogen-donor ligan (TPEN) was added into system.

The increase of metal extraction efficiency by adding of synergistic extractant was an alternatives to improve the extraction efficiency, which presented by Nishihama et al (8). They review advanced liquid-liquid extraction systems for the separation of metal ions by a combination of conversion of the metal species with chemical reaction.

5.1.2 The Effect of D2EHPA Dosage

The experiment investigated three levels of D2EHPA dosage, 10%, 20%, and 30% v/v of organic phase, which yielded average chromium extraction efficiencies of 78.07%, 79.65%, and 81.53%, respectively. After statistical analysis was performed, the average chromium extraction efficiency for D2EHPA dosage 30% v/v of organic phase was significantly different from those of 20% and 10%, respectively.

D2EHPA dosage in extraction stage had an effect to chromium extraction efficiency, which corresponded to the second hypothesis of extraction stage, which stated that, average chromium extraction efficiency at dose of D2EHPA 30% v/v of organic phase would be better than those of 20% and 10%.

The chromium extraction efficiency would be increased when the dose of D2EHPA was increased, indicated by Pandy et al (6). They reported that when D2EHPA dosage was increased from 10% to 15%, the chromium extraction efficiencies were increased from 85.2% to 95.0%. The increase of chromium extraction efficiency as a result of increasing D2EHPA dosage, which increase the active specie with ability to chelate chromium (III) ions. This leads to better extraction of chromium from aqueous phase (tanning wastewater) into organic phase.

The increase of metal extraction was also found in the research presented by Bhaskara et al (7). They investigated the use of phosphoric acid based as extractant in liquid-liquid extraction of nickel at macro-level concentration from sulphate/chloride solutions. The results indicated that nickel extraction was increased with an increase of extractant concentration. There were other researchers, which also found the increase of metal extraction when increased dose of extractant (9, 29, 30, 31, 32). They studied on metal extraction using organophosphorus acid derivatives such as Cyanex®272, as extracting agent.

5.1.3 The Effect of Extraction Time

Three levels of extraction time, 1, 3, and 6 minute(s), were studied. The average chromium extraction efficiencies were 78.02%, 79.66%, and 81.57%, respectively. From statistical analysis showed that the average chromium extraction efficiency at extraction time of 6 minutes was significantly higher than those of 3 minutes and 1 minute, respectively.

The effect of extraction time to chromium extraction efficiency corresponded to the third hypothesis of extraction stage, which stated that, the average chromium extraction efficiency at extraction time of 6 minutes would be better than those of 3 minutes and 1 minute.

The increase of chromium extraction efficiency could be explained that when increasing extraction time, the chelating agent, D2EHPA, would have longer time to extract chromium (III) ion in the emulsion, yielded higher efficiency. The effect of extraction time has the similar trend to the study of Pandy et al (6), which reported that, when increased extraction time from 30 seconds to 2 minutes, chromium extraction efficiencies increased from 90% to 95%. The increase of extraction time yielded higher metal extraction efficiency was also found in the research by Bhaskara et al (7), Lanagan et al (29), and Saji et al (30, 31, 32).

5.2 The Effect of Variables in Recovery Stage

Two variables, recovery time and NH_3 dosage, were investigated in recovery stage, The effect of each variable is described below.

5.2.1 The Effect of HCl Concentration

The experiment investigated three levels of HCl concentration, 3.6N, 4.8N, and 6.0N. The average chromium recovery efficiencies of 37.91%, 49%, and 56.78% were achieved , respectively. The statistical analysis showed that the average chromium recovery efficiency at 6.0N HCl was significant difference from those of 4.8N and 3.6N, respectively.

The effect of HCl concentration still corresponded to the first hypothesis of recovery stage, which stated that, 6.0N HCl would give higher average chromium recovery efficiency than those of 4.8N and 3.6N.

The higher concentration of HCl would increase the acidity of the emulsion, which was able to elute more chromium (III) ions from organic phase back into aqueous phase. The results were consistent with the study of Pandy et al (6), which found that chromium recovery efficiency was increased after the increase of HCl concentration from 1M to 11M. Lanagan et al (29) reported the similar results that found the increase of chromium stripping efficiency when increased concentration of HCl.

5.2.2 The Effect of Recovery Time

Three levels of recovery time, 10, 30, and 60 minutes, were studied. The average chromium recovery efficiencies were 29.84%, 56.09%, and 57.81%, respectively. From statistical analysis, it showed that the average chromium recovery efficiencies at recovery time of 60 minutes and 30 minutes were significantly different than that of 10 minutes. However, there was no significant difference between average chromium recovery efficiencies at recovery time of 60 minutes and 30 minutes.

The effect of recovery time to chromium recovery efficiency corresponded to the second hypothesis of recovery stage, which stated that the average chromium extraction efficiency at recovery time of 60 minutes would be better than those of 30 minutes and 10 minutes. However, the average chromium recovery efficiencies between recovery time of 60 minutes and 30 minutes were not significantly different.

The increase of chromium recovery efficiency could be explained that when recovery time was increased, eluting agent (which was HCl acid) would have longer time to extract chromium (III) ions in emulsion. Therefore higher efficiency was achieve. Pandy et al (6), also reported that, when recovery time was increased from 10 minutes to 30 minutes, the chromium recovery efficiencies increased approximately from 65% to 80%. Lanagan et al (29) reported the similar results that found the increase of chromium stripping efficiency when increased stripping contact time.

CHAPTER 6
CONCLUSIONS AND RECOMMENDATIONS

Research on recovery of chromium from tannery wastewater, using the solvent extraction technique was investigated. The conclusions and recommendations of the study are illustrated below.

6.1 Conclusions

The experiment consisted of two stages. The first was extraction stage that studying the effects of NH_3 dosage, D2EHPA dosage, and extraction time. And the second stage was recovery stage that studying the effects of HCl concentration and recovery time. All the experiments could be concluded as follows:

6.1.1 Conclusions in Extraction Stage

1) In extraction stage, chromium extraction efficiency was increased when extraction time increased within the studied range.

2) In extraction stage, chromium extraction efficiency was increased when D2EHPA dosage increased within the studied range.

3) In extraction stage, chromium extraction efficiency was increased when NH_3 dosage increased within the studied range.

4) From statistical analysis, the best level of studied variables in the extraction stage were 12% NH_3 (v/v of D2EHPA), 30% D2EHPA (v/v of organic phase), and extraction time of 6 minutes, which gave the average chromium extraction efficiency of 85.88%. (SD = 2.20%)

6.1.1 Conclusions in Extraction Stage

1) In recovery stage, chromium recovery efficiency was increased when recovery time increased within the studied range.

2) In recovery stage, chromium recovery efficiency was increased when HCl concentration increased within the studied range.

3) From statistical analysis, the best level of studied variables in the recovery stage were 6.0N HCl and recovery time of 30 minutes, which gave the average chromium recovery efficiency of 67.76%. (SD = 1.66%)

6.2 Recommendations

The following statements are the recommendations from the study on chromium recovery from chrome tanning wastewater using solvent extraction process.

1) Further study on other organophosphorus acid derivatives in place of D2EHPA, such as cyanex 272® or others should be investigated.

2) Further study on other synergistic extracting agent instead of NH_3, such as TPEN (*N,N,N',N'* - tetrakis(2-pyridylmethyl)ethylenediamine) or others, which are more metal selective or more effective, should be carried out.

3) Reuse of organic phase in the extraction process, which is very useful and cost effective, should be further studied.

4) Further study on continuous system and/or pilot-scale to simulate the real situation should be done.

5) Application of the solvent extraction process to other types of wastewater, such as electroplating wastewater and others should be investigated.

REFERENCES

1. AIChE America Institute of Chemical Engineers [online] Available : http://www.aiche.org/conferences/techprogram/paperdetail.asp?PaperID=29752&DSN=annual [2003, Dec 17].
2. Department of Industrial Work [online] Available : http://www.diw.go.th/ factory list.html [2001, Nov 2]
3. Tannery Industry Association [online] Available : http://www.thaitanning.org/industry.html [2001, Nov 3]
4. Wood B. Clean Technology Options in the Leather Tanning Industry. Seminar on the Profitability of Clean Technology in the Leather Tanning Industries, 20-21 October 1992, Samutprakarn, Thailand, 1992.
5. Abdel – Shafy HI et al. Decreasing the level of heavy metals by aerobic treatment of tannery wastewater. CEJOEM, 2002, 8(4): 298-309.
6. Pandey B D, et al. Extraction of chromium(III) from spent tanning baths. Hydrometallurgy, 1996, 40, 343-357.
7. Bhaskara P V R, et al. Liquid-liquid extraction of nickel at macro-level concentration from sulphate/chloride solutions using phosphoric acid based extractants. Minerals Engineering, 2002, 15, 461-464.
8. Nishihama S, et al. Review of advanced Liquid-liquid extraction systems for the separation of metal ions by a combination of conversion of the metal species with chemical reaction. Ind. Eng. Chem., 2001, 40, 3085-3091.
9. Takeshita K, et al. Solvent extraction separation of Cd(II) and Zn(II) with the organophosphorus extractant D2EHPA and the aqueous nitrogen-donor ligand TPEN. Hydrometallurgy, 2003, 70, 63-71.
10. Environmental Protection Agency [Online] Available : http://www.epa.gov . Food and Agricultural Industry. chapter 9.15.
11. ETPI Environment Technology Program for Industry. The Leather Sector. Federation of Pakistan Chamber of Pakistan (FPCCI), 1998.
12. Fabiani C, et al. Chromium (III) salts recovery process form tannery wastewater.

Desalination journal, 1996; 108: 183-161

13. Apostolos GV and Cleanthes JI. Detoxification of tannery waste liquors with an electrolysis systemm, 1997; 91(1-2): 147-152.
14. Punsawad, et al. Chromium Recovery from Tannery Industry. Lab-scale GTZ program, 2536.
15. Khwaja AR, Singh R, and Tandon SN. Monitoring of Ganga Water and tannery pollution at Kanpur (India): A case study. Journal of Env. Mon. and Ass, 2001; 68: 19-35.
16. Laconi CD, et al. Combined chemical and biological oxidation for tannery wastewater treatment. Meeting on: Biodegradation of toxic and biorefractory compounds and their impact on wastewater treatment plants, 29-30 November 2001, Rome, Italy.
17. Aravindhan R, et al. Bioaccumulation of chromium form tannery wastewater: An approach for chrome recovery and reuse. Env. Sci. Tech., 2004; 38(1), 300-306.
18. Diiaconi C, et al. Tannery wastewater treatment by sequencing batch boifilm reactor. Env. Sci. Tech, 2003; 37(14), 3199-3205.
19. Goltara A, Martinez J, and Mendez R. Carbon and Nitrogen removal from tannery wastewater with a membrane bioreactor. Wat. Sci. Tech, 2003; 48(1), 207-214.
20. NSC. Chromium and Chromium Compounds [online] Available : http://www.nsc. org /library/chemical/chromium.htm [2003, Oct 27]
21. Agency for Toxic Substances and Disease Registry (ATSDR). Toxicological profile for chromium (Update). Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service, 2000.
22. Extraction Theory [online] Available : http://www.chem.ulf.edu/~barbaro/2211L/ extraction/extraction_theory.html [2003, Nov 27]
23. Moris B S, et al. Characterisation of the reactive test system $ZnSO_4$/D2EHPA in *n*-heptane. Hydrometallurgy, [online] Available : http://www.sciencedirect. com/science?_ob=MImg&_imagekey=B6VBT-4BGHJ11-1-J&_cdi=5935 &_orig=search&_coverDate=01%2F19%2F2004&_sk=999999999&view =c&wchp=dGLbVzb-zSkzS&_acct=C000014278&_version=1

&_userid=206209&md5=802c534bcb518778ae98add4789be103&ie=f.pdf [2004, May 16].

24. Heavy Water Board, Other services. [online] Available : http://www.dae.gov.in/heavywaterboard.org/docs/services.htm [2004, May 11]
25. Principe F, et al. The solubility and stability of organophosphoric acid extractants in H_2SO_4 and HCl media. Hydrometallurgy, 2003, 68, 115-124.
26. Chulalongkorn University and Department of Industrial. Safety data sheet. [online] Available : http://www.sc.chula.ac.th/msds/eng/8141/814181.htm [2004, May 11]
27. Juang R, et al. Mechanistic analysis of solvent extraction of heavy metals in membrane contactors. Journal of Membrane Science, 2003, 213, 125-135.
28. Kongolo K, et al. Cobalt and Zinc recovery from copper sulphate solution by solvent extraction. Minerals Engineering, 2003, 16, 1371-1374.
29. Lanagen MD and Ibana DC. The solvent extraction and stripping of chromium with Cyanex® 272. Minerals Engineering, 2003; 16: 237-245.
30. John KS, et al. Solvent extraction of titanium (IV) from acidic chroride solutions by Cyanex 923. Hydrometallurgy, 1999; 51: 9-18.
31. John KS, et al. Extraction of iron (III) from acidic chroride solutions by Cyanex 923. Hydrometallurgy, 1998; 49: 289-296.
32. John KS, et al. Solvent extraction of tetravalent titanium from acidic chroride solutions by 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester. Hydrometallurgy, 1999; 53: 245-253.
33. APHA, AWWA, WPCF. Standard Methods for the Examinations of Water and Wastewater, 21st ed., Washington, D.C.: American Public Health Association. 2000.
34. Sanders D H, Statistics: a first course, international edition, USA, McGraw-Hill, 1995.
35. Green S B, Salkind N J, Akey T M, Using SPSS for windows: analysis and understanding data, 2nd ed., New Jersey, Prentice-Hall Inc., 2000.

APPENDIX A

DATA OF EXPERIMENTS

Table A-1 Chromium Extraction Efficiency from Extraction Stage

Extraction time	DEHPA dosage	NH3 dosage	Chromium Content and Chromium Extraction Efficiency										
			run 1			run 2			run 3			Mean of Efficiency	SD
(minute)	(% v/v of org.phase)	(% v/v of DEHPA)	inf	eff	efficiency	inf	eff	efficiency	inf	eff	efficiency		
1	10	4	1942.0	497.3	74.39	1994.0	532.8	73.28	2110.0	495.9	76.50	74.72	1.64
		8	1942.0	471.3	75.73	1994.0	510.9	74.38	2110.0	485.7	76.98	75.70	1.30
		12	1942.0	438.5	77.42	1994.0	484.9	75.68	2110.0	434.7	79.40	77.50	1.86
	20	4	1942.0	470.5	75.77	1994.0	505.3	74.66	2110.0	488.0	76.87	75.77	1.11
		8	1942.0	434.0	77.65	1994.0	472.6	76.30	2110.0	428.8	79.68	77.88	1.70
		12	1942.0	388.8	79.98	1994.0	433.9	78.24	2110.0	370.9	82.42	80.21	2.10
	30	4	1942.0	442.6	77.21	1994.0	476.6	76.10	2110.0	459.6	78.22	77.18	1.06
		8	1942.0	390.0	79.92	1994.0	427.3	78.57	2110.0	384.2	81.79	80.09	1.62
		12	1942.0	327.6	83.13	1994.0	371.1	81.39	2110.0	321.1	84.78	83.10	1.70
3	10	4	1942.0	474.4	75.57	1994.0	509.3	74.46	2110.0	466.5	77.89	75.97	1.75
		8	1942.0	428.8	77.92	1994.0	467.2	76.57	2110.0	421.4	80.03	78.17	1.74
		12	1942.0	376.7	80.6	1994.0	421.5	78.86	2110.0	368.2	82.55	80.67	1.85
	20	4	1942.0	440.8	77.3	1994.0	474.8	76.19	2110.0	436.6	79.31	77.60	1.58
		8	1942.0	412.5	78.76	1994.0	450.4	77.41	2110.0	424.7	79.87	78.68	1.23
		12	1942.0	343.9	82.29	1994.0	387.8	80.55	2110.0	332.1	84.26	82.37	1.86
	30	4	1942.0	408.2	78.98	1994.0	441.3	77.87	2110.0	429.6	79.64	78.83	0.89
		8	1942.0	376.2	80.63	1994.0	413.2	79.28	2110.0	373.9	82.28	80.73	1.50
		12	1942.0	307.0	84.19	1994.0	349.9	82.45	2110.0	313.8	85.13	83.92	1.36
6	10	4	1942.0	415.4	78.61	1994.0	460.4	76.91	2110.0	407.0	80.71	78.74	1.90
		8	1942.0	389.2	79.96	1994.0	437.5	78.06	2110.0	405.3	80.79	79.60	1.40
		12	1942.0	351.1	81.92	1994.0	404.4	79.72	2110.0	357.9	83.04	81.56	1.69
	20	4	1942.0	396.2	79.6	1994.0	443.9	77.74	2110.0	398.8	81.10	79.48	1.68
		8	1942.0	353.2	81.81	1994.0	400.8	79.90	2110.0	330.2	84.35	82.02	2.23
		12	1942.0	325.5	83.24	1994.0	373.3	81.28	2110.0	338.7	83.95	82.82	1.38
	30	4	1942.0	365.5	81.18	1994.0	413.6	79.26	2110.0	373.9	82.28	80.91	1.53
		8	1942.0	315.4	83.76	1994.0	363.9	81.75	2110.0	340.6	83.86	83.12	1.19
		12	1942.0	272.9	85.95	1994.0	326.0	83.65	2110.0	252.1	88.05	85.88	2.20

Table A-2 Chromium Recovery Efficiency from Recovery Stage

Recovery time	HCl concecn-tration	Chromium Content and Chromium Recovery Efficiency										
		run 1			run 2			run 3			Mean of Efficiency	SD
(minute)	(N)	inf	eff	efficiency	inf	eff	efficiency	inf	eff	efficiency		
10	3.6	1572.0	341.9	21.75	1614.1	361.6	22.40	1708.0	413.3	24.20	22.78	1.27
	4.8	1572.0	473.5	30.12	1614.1	503.9	31.22	1708.0	565.7	33.12	31.49	1.52
	6.0	1572.0	523.6	33.31	1614.1	568.3	35.21	1708.0	635.5	37.21	35.24	1.95
30	3.6	1572.0	663.9	42.23	1614.1	693.6	42.97	1708.0	765.0	44.79	43.33	1.32
	4.8	1572.0	873.2	55.55	1614.1	917.8	56.86	1708.0	1009.4	59.10	57.17	1.80
	6.0	1572.0	1037.7	66.01	1614.1	1097.1	67.97	1708.0	1183.8	69.31	67.76	1.66
60	3.6	1572.0	733.2	46.64	1614.1	768.1	47.59	1708.0	830.9	48.65	47.63	1.01
	4.8	1572.0	900.4	57.28	1614.1	947.8	58.72	1708.0	1014.4	59.39	58.46	1.08
	6.0	1572.0	1027.6	65.37	1614.1	1085.8	67.27	1708.0	1184.7	69.36	67.33	2.00

APPENDIX B
STATISTICAL ANALYSIS RESULTS

Table B-1 The Statistical Hypotheses and the Interpretation from the Results, at 0.05 level of Significance

Statistical Analysis	Statistical Hypotheses		Significant	Interpretation
Test of Normality	H_0:	normal distribution	P-value > 0.05	Data was normal distribution
	H_1:	non normal distribution	P-value $\leq$ 0.05	Data was not normal distribution
Test of Homogeneity of Variance	H_0:	$\sigma_1^2 = \sigma_2^2$	P-value > 0.05	Variances were homogeneity
	H_1:	$\sigma_1^2 \neq \sigma_2^2$	P-value $\leq$ 0.05	Variances were not homogeneity
Means Comparison	H_0:	$\mu_1 = \mu_2$	P-value > 0.05	Means were not different
	H_1:	$\mu_1 \neq \mu_2$	P-value $\leq$ 0.05	Means were different
Correlation Analysis	H_0:	$\rho = 0$	P-value > 0.05	Both variables were not correlated
	H_1:	$\rho \neq 0$	P-value $\leq$ 0.05	Both variables were correlated
Regression Analysis	H_0:	$\beta = 0$	P-value > 0.05	Independent variable had no effect to dependent variable
	H_1:	$\beta \neq 0$	P-value $\leq$ 0.05	Independent variable had effect to dependent variable

Table B-2 The Test of Normality of Chromium Extraction Efficiency at Different NH_3 Dosages

		Kolmogorov-Smirnov(a)			Shapiro-Wilk		
	NH3 Dosage	Statistic	df	Sig.	Statistic	df	Sig.
Chromium Extraction Efficiency	4 %v/v of D2EHPA	.057	27	.200(*)	.987	27	.975
	8 %v/v of D2EHPA	.092	27	.200(*)	.983	27	.916
	12 %v/v of D2EHPA	.097	27	.200(*)	.992	27	.998

* This is a lower bound of the true significance.

a Lilliefors Significance Correction

Table B-3 The Test of Homogeneity of Variance of Chromium Extraction Efficiency at Different NH_3 Dosages

		Levene Statistic	df1	df2	Sig.
Chromium Extraction Efficiency	Based on Mean	.300	2	78	.741

Table B-4 The one-way ANOVA of Average Chromium Extraction Efficiency at Different NH_3 Dosages

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	252.954	2	126.477	19.752	<0.001
Within Groups	499.459	78	6.403		
Total	752.413	80			

Table B-5 The LSD's Multiple Comparison of Average Chromium Extraction Efficiency at Different NH_3 Dosages

					95% Confidence Interval	
(I) NH_3 Dosage	(J) NH_3 Dosage	Mean Difference (I-J)	Std. Error	Sig.	Lower Bound	Upper Bound
4 %v/v of D2EHPA	8 %v/v of D2EHPA	-1.86630(*)	.68871	.008	-3.2374	-.4952
	12 %v/v of D2EHPA	-4.31556(*)	.68871	<0.001	-5.6867	-2.9444
8 %v/v of D2EHPA	4 %v/v of D2EHPA	1.86630(*)	.68871	.008	.4952	3.2374
	12 %v/v of D2EHPA	-2.44926(*)	.68871	.001	-3.8204	-1.0781
12 %v/v of D2EHPA	4 %v/v of D2EHPA	4.31556(*)	.68871	<0.001	2.9444	5.6867
	8 %v/v of D2EHPA	2.44926(*)	.68871	.001	1.0781	3.8204

* The mean difference is significant at the .05 level.

Table B-6 The Test of Normality of Chromium Extraction Efficiency at Different D2EHPA Dosages

		Kolmogorov-Smirnov(a)			Shapiro-Wilk		
	D2EHPA Dosage	Statistic	df	Sig.	Statistic	df	Sig.
Chromium Extraction Efficiency	10 %v/v of org phase	.072	27	.200(*)	.977	27	.800
	20 %v/v of org phase	.092	27	.200(*)	.971	27	.632
	30 %v/v of org phase	.082	27	.200(*)	.988	27	.986

* This is a lower bound of the true significance.

a Lilliefors Significance Correction

Table B-7 The Test of Homogeneity of Variance of Chromium Extraction Efficiency at Different D2EHPA Dosages

		Levene Statistic	df1	df2	Sig.
Chromium Extraction Efficiency	Based on Mean	.099	2	78	.906

Table B-8 The one-way ANOVA of Average Chromium Extraction Efficiency at Different D2EHPA Dosages

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	161.866	2	80.933	10.690	<0.001
Within Groups	590.547	78	7.571		
Total	752.413	80			

Table B-9 The LSD's Multiple Comparison of Average Chromium Extraction Efficiency at Different D2EHPA Dosages

					95% Confidence Interval	
(I) D2EHPA Dosage	(J) D2EHPA Dosage	Mean Difference (I-J)	Std. Error	Sig.	Lower Bound	Upper Bound
10 %v/v of org phase	20 %v/v of org phase	-1.57593(*)	.74888	.039	-3.0668	-.0850
	30 %v/v of org phase	-3.45815(*)	.74888	<0.001	-4.9491	-1.9672
20 %v/v of org phase	10 %v/v of org phase	1.57593(*)	.74888	.039	.0850	3.0668
	30 %v/v of org phase	-1.88222(*)	.74888	.014	-3.3731	-.3913
30 %v/v of org phase	10 %v/v of org phase	3.45815(*)	.74888	<0.001	1.9672	4.9491
	20 %v/v of org phase	1.88222(*)	.74888	.014	.3913	3.3731

* The mean difference is significant at the .05 level.

Table B-10 The Test of Normality of Chromium Extraction Efficiency at Different Extraction Times

		Kolmogorov-Smirnov(a)			Shapiro-Wilk		
	Extraction Time	Statistic	df	Sig.	Statistic	df	Sig.
Chromium Extraction Efficiency	1 minute	.106	27	.200(*)	.963	27	.438
	3 minute	.101	27	.200(*)	.979	27	.828
	6 minute	.076	27	.200(*)	.981	27	.894

* This is a lower bound of the true significance.

a Lilliefors Significance Correction

Table B-11 The Test of Homogeneity of Variance Chromium Extraction Efficiency at Different Extraction Times

		Levene Statistic	df1	df2	Sig.
Chromium Extraction Efficiency	Based on Mean	.247	2	78	.782

Table B-12 The one-way ANOVA of Average Chromium Extraction Efficiency at Different Extraction Times

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	170.950	2	85.475	11.466	<0.001
Within Groups	581.463	78	7.455		
Total	752.413	80			

Table B-13 The LSD's Multiple Comparison of Average Chromium Extraction Efficiency at Different Extraction Times

					95% Confidence Interval	
(I) Extraction Time	(J) Extraction Time	Mean Difference (I-J)	Std. Error	Sig.	Lower Bound	Upper Bound
1 minute	3 minute	-1.64444(*)	.74310	.030	-3.1238	-.1650
	6 minute	-3.55519(*)	.74310	<0.001	-5.0346	-2.0758
3 minute	1 minute	1.64444(*)	.74310	.030	.1650	3.1238
	6 minute	-1.91074(*)	.74310	.012	-3.3901	-.4313
6 minute	1 minute	3.55519(*)	.74310	<0.001	2.0758	5.0346
	3 minute	1.91074(*)	.74310	.012	.4313	3.3901

* The mean difference is significant at the .05 level.

Table B-14 The Pearson Correlation of Chromium Extraction Efficiency and NH_3 Dosage

		Chromium Extraction Efficiency	NH_3 Dosage
Chromium Extraction Efficiency	Pearson Correlatison	1	.578(**)
	Sig. (2-tailed)	.	<0.001
	N	81	81
NH_3 Dosage	Pearson Correlation	.578(**)	1
	Sig. (2-tailed)	<0.001	.
	N	81	81

** Correlation is significant at the 0.01 level (2-tailed).

Table B-15 The Pearson Correlation of Chromium Extraction Efficiency and D2EHPA Dosage

		Chromium Extraction Efficiency	D2EHPA Dosage
Chromium Extraction Efficiency	Pearson Correlation	1	.463(**)
	Sig. (2-tailed)	.	<0.001
	N	81	81
D2EHPA Dosage	Pearson Correlation	.463(**)	1
	Sig. (2-tailed)	<0.001	.
	N	81	81

** Correlation is significant at the 0.01 level (2-tailed).

Table B-16 The Pearson Correlation of Chromium Extraction Efficiency and Extraction Time

		Chromium Extraction Efficiency	Extraction Time
Chromium Extraction Efficiency	Pearson Correlation	1	.475(**)
	Sig. (2-tailed)	.	<0.001
	N	81	81
Extraction Time	Pearson Correlation	.475(**)	1
	Sig. (2-tailed)	<0.001	.
	N	81	81

** Correlation is significant at the 0.01 level (2-tailed).

Table B-17 The Model Summary from Stepwise Multiple Regression of Independent Variables (NH_3 Dosage, D2EHPA Dosage, and Extraction Time) to Dependent Variable (Chromium Extraction Efficiency)

Model	Variables Entered	Variables Removed	Method	R	R Square	Adjusted R Square	Std. Error of the Estimate
1	NH_3 Dosage		Stepwise (Criteria: Probability-of-F-to-enter <= .050, Probability-of-F-to-remove >= .100).	.578 (a)	.334	.326	2.51826
2	Extraction Time		Stepwise (Criteria: Probability-of-F-to-enter <= .050, Probability-of-F-to-remove >= .100).	.748 (b)	.560	.549	2.05974
3	D2EHPA Dosage		Stepwise (Criteria: Probability-of-F-to-enter <= .050, Probability-of-F-to-remove >= .100).	.880 (c)	.775	.766	1.48356

a Predictors: (Constant), NH_3 Dosage

b Predictors: (Constant), NH_3 Dosage, Extraction Time

c Predictors: (Constant), NH_3 Dosage, Extraction Time, D2EHPA Dosage

Table B-18 The Stepwise Multiple Regression of Independent Variables (NH_3 Dosage, D2EHPA Dosage, and Extraction Time) to Dependent Variable (Chromium Extraction Efficiency)

Model		Unstandardized Coefficients		Standardized Coefficients	t	Sig.
		B	Std. Error	Beta		
1	(Constant)	75.434	.740		101.897	<0.001
	NH_3 Dosage	.539	.086	.578	6.297	<0.001
2	(Constant)	73.083	.710		102.896	<0.001
	NH_3 Dosage	.539	.070	.578	7.698	<0.001
	Extraction Time	.705	.111	.475	6.331	<0.001
3	(Constant)	69.625	.652		106.832	<0.001
	NH_3 Dosage	.539	.050	.578	10.688	<0.001
	Extraction Time	.705	.080	.475	8.790	<0.001
	D2EHPA Dosage	.173	.020	.463	8.565	<0.001

Table B-19 The Test of Normality of Chromium Recovery Efficiency at Different HCl Concentrations

		Kolmogorov-Smirnov(a)			Shapiro-Wilk		
	HCl Concentration	Statistic	df	Sig.	Statistic	df	Sig.
Chromium Recovery Efficiency	3.6 N	.312	9	.012	.772	9	.010
	4.8 N	.355	9	.002	.708	9	.002
	6.0 N	.368	9	.001	.705	9	.002

* This is a lower bound of the true significance.

a Lilliefors Significance Correction

Table B-20 The Test of Homogeneity of Variance of Chromium Recovery Efficiency at Different HCl Concentrations

		Levene Statistic	df1	df2	Sig.
Chromium Recovery Efficiency	Based on Mean	1.750	2	24	.195

Table B-21 The Kruskal-Wallis H test of Average Chromium Recovery Efficiency at Different HCl Concentrations

	HCl Concentration	N	Mean Rank	Chi-Square	df	Asymp. Sig.
Chromium Recovery Efficiency	3.0	9	9.00	7.143	2	.028
	4.0	9	14.00			
	6.0 N	9	19.00			
	Total	27				

Table B-22 The Mann-Whitney U test of Average Chromium Recovery Efficiency at HCl Concentrations 3.6N and 4.8N

	HCl Conc.	N	Mean Rank	Sum of Ranks	Mann-Whitney U	Wilcoxon W	Z	Asymp. Sig. (2-tailed)	Exact Sig. [2*(1-tailed Sig.)]
Chromium Recovery Efficiency	3.6 N	9	7.00	63.00	18.000	63.000	-1.987	.047	.050(a)
	4.8 N	9	12.00	108.00					
	Total	18							

a Not corrected for ties.

Table B-23 The Mann-Whitney U test of Average Chromium Recovery Efficiency at HCl Concentrations 4.8N and 6.0N

	HCl Conc.	N	Mean Rank	Sum of Ranks	Mann-Whitney U	Wilcoxon W	Z	Asymp. Sig. (2-tailed)	Exact Sig. [2*(1-tailed Sig.)]
Chromium Recovery Efficiency	4.8 N	9	7.00	63.00	18.000	63.000	-1.987	.047	.050(a)
	6.0 N	9	12.00	108.00					
	Total	18							

a Not corrected for ties.

Table B-24 The Mann-Whitney U test of Average Chromium Recovery Efficiency at HCl Concentrations 3.6N and 6.0N

	HCl Conc.	N	Mean Rank	Sum of Ranks	Mann-Whitney U	Wilcoxon W	Z	Asymp. Sig. (2-tailed)	Exact Sig. [2*(1-tailed Sig.)]
Chromium Recovery Efficiency	3.6 N	9	7.00	63.00	18.000	63.000	-1.987	.047	.050(a)
	6.0 N	9	12.00	108.00					

	Total	18

a Not corrected for ties.

Table B-25 The Test of Normality of Chromium Recovery Efficiency at Different Recovery Times

		Kolmogorov-Smirnov(a)			Shapiro-Wilk		
	Recovery Time	Statistic	df	Sig.	Statistic	df	Sig.
Chromium Recovery Efficiency	10 minute	.186	9	.200(*)	.904	9	.275
	30 minute	.188	9	.200(*)	.892	9	.210
	60 minute	.189	9	.200(*)	.907	9	.298

* This is a lower bound of the true significance.

a Lilliefors Significance Correction

Table B-26 The Test of Homogeneity of Variance of Chromium Recovery Efficiency at Different Recovery Times

		Levene Statistic	df1	df2	Sig.
Chromium Recovery Efficiency	Based on Mean	1.754	2	24	.195

Table B-27 The one-way ANOVA of Average of Chromium Recovery Efficiency at Different Recovery Times

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	4423.025	2	2211.513	29.927	<0.001
Within Groups	1773.501	24	73.896		
Total	6196.526	26			

Table B-28 The LSD's Multiple Comparison of Average Chromium Recovery Efficiency at Different Recovery Times

					95% Confidence Interval	
(I) Recovery Time	(J) Recovery Time	Mean Difference (I-J)	Std. Error	Sig.	Lower Bound	Upper Bound
10 minute	30 minute	-26.25000(*)	4.05232	<0.001	-34.6136	-17.8864
	60 minute	-27.97000(*)	4.05232	<0.001	-36.3336	-19.6064
30 minute	10 minute	26.25000(*)	4.05232	<0.001	17.8864	34.6136
	60 minute	-1.72000	4.05232	.675	-10.0836	6.6436
60 minute	10 minute	27.97000(*)	4.05232	<0.001	19.6064	36.3336
	30 minute	1.72000	4.05232	.675	-6.6436	10.0836

* The mean difference is significant at the .05 level.

Table B-29 The Spearman Correlation of Chromium Recovery Efficiency and HCl Concentration

		Chromium Recovery Efficiency	NH3 Dosage
Chromium Recovery Efficiency	Correlation Coefficient	1.000	.524(**)
	Sig. (2-tailed)	.	.005
	N	27	27
HCl Concentration	Correlation Coefficient	.524(**)	1.000
	Sig. (2-tailed)	.005	.
	N	27	27

** Correlation is significant at the 0.01 level (2-tailed).

Table B-30 The Pearson Correlation of Chromium Recovery Efficiency and Recovery Time

		Chromium Recovery Efficiency	Recovery Time
Chromium Recovery Efficiency	Pearson Correlation	1	.705(**)
	Sig. (2-tailed)	.	<0.001
	N	27	27
Recovery Time	Pearson Correlation	.705(**)	1
	Sig. (2-tailed)	<0.001	.
	N	27	27

** Correlation is significant at the 0.01 level (2-tailed).

Table B-31 The Model Summary from Stepwise Multiple Regression of Independent Variables (HCl Concentration and Recovery Time) to Dependent Variable (Chromium Recovery Efficiency)

Model	Variables Entered	Variables Removed	Method	R	R Square	Adjusted R Square	Std. Error of the Estimate
1	Recovery Time		Stepwise (Criteria: Probability-of-F-to-enter <= .050, Probability-of-F-to-remove >= .100).	.705 (a)	.497	.477	11.16561
2	HCl Concentration		Stepwise (Criteria: Probability-of-F-to-enter <= .050, Probability-of-F-to-remove >= .100).	.869 (b)	.756	.735	7.94511

a Predictors: (Constant), Recovery Time

b Predictors: (Constant), Recovery Time, HCl Concentration

Table B-32 The Stepwise Multiple Regression of Independent Variables (HCl Concentration and Recovery Time) to Dependent Variable (Chromium Recovery Efficiency)

Model		Unstandardized Coefficients		Standardized Coefficients	t	Sig.
		B	Std. Error	Beta		
1	(Constant)	30.586	4.095		7.469	<0.001
	Recovery Time	.520	.105	.705	4.970	<0.001
2	(Constant)	-7.148	8.037		-.889	.383
	Recovery Time	.520	.074	.705	6.985	<0.001
	HCl Concentration	7.861	1.561	.508	5.037	<0.001

BIOGRAPHY

NAME	Mr. Pisachai Yooprasert
DATE OF BITRH	September, 27 1980
PLACE OF BIRTH	Samutsongkhram, Thailand
INSTITUTIONS ATTENDED	Chiang Mai University, 1999; Bachelor of Science (Chemistry) Mahidol University, 2004; Master of Science (Environmental Technology)
RESEARCH GRANT	Post-Graduate Education, Training and Research Program in Environmental Science Technology and Management under Higher Education Development Project of the Ministry of University Affairs
HOME ADDRESS	49 m.10 Bangkuntak, Muang District, Samutsongkhram, 75000