

CHROMIUM REMOVAL FROM CHELTECH (ZARIA) TANNERY

EFFLUENT AS A FORM OF EFFLUENT TREATMENT

**A THESIS PRESENTED TO THE POSTGRADUATE SCHOOL
AHMADU BELLO UNIVERSITY, ZARIA**

BY

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M.Sc / ENG / 17455 / 98-99**

**IN PARTIAL FULFILMENT OF THE REQUIREMENTS
FOR THE DEGREE OF MASTERS OF SCIENCE IN
CHEMICAL ENGINEERING**

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AUGUST, 2004.

DECLARATION

I, BUBA, MATTHEW ADAMU, declares that this thesis is solely the result of my work and has never been submitted any where for any degree. All literature cited have been duly acknowledged in the references. I take full responsibility for any mistakes or misrepresentations that may occur.

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CERTIFICATION

This project is titled “CHROMIUM REMOVAL FROM CHELTECH (ZARIA) TANNERY EFFLUENT ” by BUBA, MATTHEW ADAMU meets the regulations governing the award of the degree of Master of Science (Chemical Engineering) of Ahmadu Bello University, Zaria, and it is approved for its contribution to knowledge and literary presentation.

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DEDICATION

This project is dedicated to Abigail Chat Olamide Buba.

ACKNOWLEDGMENT

I am grateful to the Almighty God for His grace and encouragement during this work.

I express my profound gratitude to my supervisors, Dr. J.O. Bello and Dr. B.O. Aderemi for their encouragement and keen interest that saw this work through.

I also wish to thank Dr. A.S. Ahmed, Head of Chemical Engineering Department for his keen interest and suggestions at various stages of this work.

I wish to thank CHELTECH staff especially Dr. P.O. Ukoha, Mr. P. Y. Garba and many others for rendering one assistance or the other, especially Mary Oyewo for the pain and understanding in typing this work.

I am grateful to my wife Kehinde Buba and Children for their patience, understanding and encouragement.

ABSTRACT

Chrome is an indispensable input in chemical tanning of pelt. For mass transfer reasons, not more than 80% of the chrome feed is absorbed by the leather leaving a balance of over 20% in the effluent. This leads to material loss if disposed untreated. In addition, the attendant possible oxidation of chromium (III) to chromium (VI) (in the presence of manganese (IV) oxide or under alkaline conditions) known for its carcinogenic effect, makes it necessary to remove good part of the chrome from the effluent before its disposal to sewers or surface water.

In this work, treatment CHELTECH (Zaria) tannery's 'mixed effluent' with varying amount of MgO (10 – 60 mg/l) at different contacting times (15 – 120 minutes) reduced the concentration of chromium in the effluent from 29.86 to 0.06 mg/l. This is equivalent to 99.8% chromium removal. The 0.06 mg/l minimum chromium concentration value in the treated effluent falls within the recommended limit for discharge into sewers and surface waters.

Chromium recovered from the mixed effluent is known to produce hard leather due to the presence of lime in the effluent. Therefore, segregated spent chromium effluent was treated with varying amount of MgO (50 – 900 mg/l) for 30 minutes. This was able to reduce the chromium

from 7020 to 982 mg/l, which is equivalent to 86% chromium removal. The effect of varying contacting time (15 – 75 minutes) using 400 mg/l of MgO reduced the amount of chromium in the effluent by 89.3%.

Treatment of the segregated spent chromium effluent offers an effective recovery, as 6268.9 mg/l of chromium was removed as against 29.80 mg/l for mixed effluent using the same process.

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LIST OF ABBREVIATIONS

BOD ₅	-	Biochemical Oxygen Demand
CHELTECH	-	Federal College of Chemical and Leather Technology
COD	-	Chemical Oxygen Demand
DS	-	Dissolved Solids
FEPA	-	Federal Environmental Protection Agency
SS	-	Suspended Solids
TS	-	Total Solids

Chapter 1

1.0 INTRODUCTION

Tanning is the key operation that transforms raw skins into leather, (Booker and Priestly (1994)). This operation dates back to some three thousand (3000) years; however, the science of leather tanning is largely a product of the twentieth century. The actual tanning procedure employed by different tanneries is quite varied, e.g. vegetable and mineral tanning, hence little standardization of unit processes has been achieved.

Tanning and finishing of leather in the mechanized way in Nigeria started in Kano, in 1949 and currently not less than 32 tanneries have been established in the country. The installed capacity of the tanneries for the production of wet-blue leather is above 8.5 million kilograms (17 million pieces) per annum, which is equivalent to 80 million square feet. If processed to finished leather, this will earn the country about 200 million US Dollars per annum at the selling price of 2.5 Dollars per square foot. Were all the hides and skins processed in Nigeria to leather and the leather subsequently converted to footwear, the total foreign exchange earning will amount to 600 million US Dollars per annum, (Paiko, (2002)).

The economic benefit derived from the leather industries are enormous. However, the negative environmental impact of its wastewater is a major setback (Rao et al (1997)). The liquid effluent discharged from the leather tanneries is large in volume, extremely putrescible and difficult to treat in a satisfactory and economical manner. The quality of wastes discharged depends on the type of tanning procedure utilized (vegetable or mineral), but more specifically affected by the operations within individual tanneries (O'Flaherty et al (1978)).

Effluents from tannery can be divided into two classes viz;

1. Continuous discharge

2. Intermittent discharge

The first constitutes a large portion of the total waste, but are not highly contaminated. While the later, though small is grossly contaminated and produces most of the pollutional effect of tannery wastes (O'Flaherty et al (1978)).

Materials which appear in tannery waste may include the following items: bits of flesh, hides scraps, hair, blood, manure, earth, salts soluble proteins, suspended lime, sulphites and sulphides, amines, chrome, arsenic, tannins, soda ash, sugars, starches, oils, fats and dyes and other organic and inorganic compounds (O'Flaherty et al (1978)).

The nature and high concentration of these contaminants in the effluent made it mandatory for tannery effluent to be treated before discharged into receiving waters. Waste from vegetable method of tanning comprises of 85 – 95% from beamhouse and 5 – 15% from tanning and finishing operations. In contrast, for chrome tanning process, 55 – 65% of the waste comes from the beamhouse and the remaining from tanning and finishing operations. This implies that the greater proportion of the waste comes from the beamhouse.

Chrome tanning waste streams have attracted much attention. This is because currently used commercial basic chromium salts and tanning methods generally afford an uptake of only 50 – 70% chrome. This poor uptake results in material wastage on one hand and ecological imbalance on

the other. The international specification for the discharge of chrome bearing streams is less than 2 ppm, (Rao et al (1997)).

In addition, the sulphides produce smell and in acid media liberate poisonous hydrogen sulphide gas, which greatly reduces biochemical oxygen content of water, that is essential to fresh water life. The gas also corrodes the vessels, so it is unacceptable for discharge to the environment untreated.

The high pollution content of tannery effluent and the adverse effect it has on the environment, coupled with government legislation on effluent limits to be discharged into sewers, waters, air and land make it necessary for tannery effluent to be treated before discharge. Treatment methods may be physical (screening, sedimentation, filtration etc), chemical (flocculation, coagulation etc) or biological (trickling filters, activated sludge, lagoons etc) (O'Flaherty et al (1978)).

Novel processes have also been developed that recycle some of the materials and waters and also recover some salts from the water before discharge. These include:

- (1) The lime – ferrous sulphate – oxidation system, (Wachsmann (1978)).
- (2) The sirofloc sewage treatment process, (Booker and Priestly (1994)).
- (3) Idronova – Hüni Plant,(Wachsmann (1978))

(4) Sulphur recovery system, (Van Groenestijn (1999)) etc.

A survey of some tanneries in Nigeria shows that most companies carry out marginal treatment of their waste by sedimentation, [Babatunde (1980) and Lawal and Singh (1983)]. The resultant effluent is then discharged into public sewers or land, which has been proved to be highly contaminated. With current campaign and clamour by communities to safeguard their environment, the government is forced to enact and enforce laws in respect to effluent standards before discharge to the environment. For example the Kano State Environmental Protection Agency is currently doing that in Kano.

The Federal College of Chemical and Leather Technology (CHELTECH), Zaria achieved full autonomy from The National Research Institute for Chemical Technology (NARICT), Zaria in 1992. The objectives of the college are:-

1. The production of high level and middle level manpower in leather and chemical technologies necessary for the leather and chemical industries for the economic development of Nigeria.
2. The identification and solution of technological problems and the needs of the leather and chemical industries in Nigeria.
3. The production of technicians and technologists for direct employment in the leather and chemical industries in Nigeria.
4. The production of technicians and technologist who have sufficient knowledge in the field and confident to engage in self-employment through entrepreneurship.

To achieve the above objectives in the field of leather technology, the college built a pilot tannery to develop skill and expertise in tannage for both staff and students. The pilot tannery is to process 250 kg of hides and skins per day. The tannery comprises of the Beamhouse, Tanyard and the Finishing sections. A large volume of effluent containing high content of contaminants bedevils this tannery, like any other tannery. The need for treating this effluent before discharge into sewers therefore becomes highly necessary.

An investigation into possible method of recovering chromium salts, fats/oils, and dyestuff from CHELTECH wastes as a form of effluent treatment was conducted by Omumene (1978). Results obtained showed that 0.3313% chromium, 2% oil and 33 gm/l of dyestuff were recovered from the tannery effluent. Benedio (1980) in his evaluation of chromium oxide content of tanyard wastewater from Holts Nigeria Tanneries Kano, also developed a process to recycle chrome liquor as a form of treatment. The process precipitated and recovered chromium hydroxides from the tannery effluent, and redissolved it in concentrated sulphuric acid to form chrome liquor for use in the tannery. The amount of chrome recovered from 3 gm/l of tannery effluent was found to be 0.081g/l, which is 2.7% recovery. These results show the inadequacy of this process at addressing the tannery effluent problem.

Ahmed and Beecroft, (1987) in their study of wastewater from Peugeot Automobile Nigeria (PAN) Limited showed that among other heavy metals found, the waste water contained chromium in its trivalent and hexavalent form. The value of the hexavalent was found to be above the recommended limit for discharge into sewers and surface water. Beecroft and Ahmed (1987) also carried out wastewater

treatment of Peugeot Automobile Nigerian (PAN) Limited, Kaduna with respect to removal of metal ions such as chromium, zinc, copper and lead. A combination of lime and alum and lime alone were used for the treatment process using the Jar – test apparatus. Chromium removal of 85% was attained, which shows the potency of the process. Chromium recovered by this process suffers a set back for reuse in the tannery because conventional methods require the precipitate obtained to be dissolved in sulphuric acid to obtain the chromium liquor for tanning. When this is done, gypsum will be formed, which when used for tanning of leather will produce undesirable hard leather.

The aim of this work is to ascertain the amount of pollutant in the tannery effluent of Federal College of Chemical and Leather technology (CHELTECH), Zaria and to treat the effluent using magnesium oxide to precipitate the chromium, as a form of effluent treatment. This is with the view that the chromium removed will be used in the tannery. It is believed that this will safeguard our environment from the pollutional effects of tannery waste and in the end reduce cost of production as chrome reclaimed can be used to supplement fresh chrome input.

2.0. LITERATURE REVIEW

2.1. Tanning Processes

Tanning may be defined as the treatment of hides and skins for preservation and conversion into useful articles of commerce. There is a vast array of tanning methods and materials and the choice depends chiefly on the properties required in the finished leather, the cost of the alternative materials, the plant available, and the type of raw material. The tanning processes are carried out in a tannery. These processes can be divided into three basic operations, which are listed below;

1. Beam house operations
2. Tanyard operations
3. Finishing operations

These are briefly considered below

2.1.1. The beamhouse operations:

The term “beamhouse” refers to the processes in the tannery between the removal of the skins or hides from storage and their preparation for tanning. This preparation includes soaking, trimmings, fleshing, unhairing,

liming and bating. These operations are of tremendous importance in the ultimate quality of the leather.

The beamhouse operations have the distinction of being the most disagreeable step in leather manufacture. It involves the use of bad smelling chemicals, which have been responsible for much of the poor name of the leather industry in its community relations.

There are four major steps involved in beamhouse operations: Soaking, unhairing, bating and pickling. These steps are common to all types of leather produced, although there are significant variations depending upon the type of skin used and the type of leather to be made. All these four steps are closely related and interdependent (Thorstensen (1993)). These steps are discussed below.

2.1.1.1. Soaking

Hides and skins are received in the tannery in the following conditions according to the source of their supplies;

- i. Green or fresh, just after flaying
- ii. Wet - salted
- iii. Dry - Salted
- iv. Dry.

These hides and skin use in leather manufacture are first soaked in water. The soaking accomplishes;

- i. Cleaning of the hides and skin from dirt, blood, and most of all salt used in curing.
- ii. Softening and swelling
- iii. Dispersal and removal of inter-fibrillary proteins which otherwise cement the fibre together and prevent their thorough rehydration.

To speed up the water uptake of the skin and reduce the chance of putrefaction, soaking is carried out in three ways.

- i. Mechanical action: This can be carried out by either vigorously circulating the water round the skin, by kneading or by flexing the skin in water. Equipment such as Rocking frame, paddles and drums can be used.
- ii. Temperature control: Warming speeds up soaking, but care must be taken not to exceed 38°C as protein fibre tends to shrink, giving thick inflexible leather.
- iii. Chemical Additions: Protein fibre absorbs water and swell more readily in acid or alkaline solution. These also help the

dispersion of inter-fibrillary proteins. Some of the chemicals added are given below;

- a. Acids e.g. formic acid, hydrochloric or sulphuric acid in 1 – 2 parts per 1000 of soaking water at 16 °C. This is used for hair saving processes.
- b. Alkalis e.g. caustic soda, soda ash, washing soda or borax in 1 – 3 parts per 1000 of soaked liquor. Others include; sodium polysulphide, ammonia liquor.
- c. Salt e.g. sodium chloride solution (3% w/v)
- d. Wetting agents e.g. detergent. (Sharphouse (1983)).

2.1.1.2. Unhairing

The aim of unhairing and liming is to remove the hair, epidermis, to some degree, the inter-fibrillary proteins and to prepare the hide or skin for removal of loose flesh and fat by the fleshing process. This may be accomplished by a number of different means, involving widely different principles of operation. Some of these are given below:

1. Sweating: This is the process whereby soaked skins are hung in dark humid rooms in a warm condition of 21 – 27 °C until the wool is loosed by bacterial activity. Water is extracted from

this wool and then dried in counter current wool drier to 16% moisture content, in which condition it is marketed.

2. Enzyme Unhairing: Soaked skins are paddled or drained occasionally in a water float at 28 – 30°C with 1 – 2% of the specific enzyme preparation at pH 8-9 for 4 hours. This is a controlled process of dewooling compared to sweating. To inhibit the activity of stray bacteria, 0.2% (w/w) sodium chlorite is added.
3. Paint unhairing: The washed or soaked skins are piled to drain off surplus water and then painted, swapped or sprayed on the flesh side with a “paint” which resembles thick “lime wash” and may be made from approximately 50 parts hydrated lime, 50 parts water and 5 – 20 parts sodium sulphide (fused). The sodium sulphide and such lime as dissolved in the water enter the skin from the flesh side, penetrating through the corium, and dissolves the young keratin cells, which enclose the hair roots. This process may take 5 – 12 hrs or longer depending on the thickness of the skin, the tightness of the fibre structure and the amount of flesh or fat left on the skin. Alternative materials that can be used include sodium hydrosulphide, calcium sulphide, or arsenic sulphide.

2.1.1.3. Bating

The delimed pelt (processed hide and skin), obtained by washing off lime with water or by chemical deliming using organic acids (boric acid, lactic acid or acetic acid), acid salts (sodium bisulphate) and salts of weak alkalis (ammonium chloride, ammonium sulphate) is prepared for bating.

Bating is the treatment of delimed pelt with enzymes preparations to remove non-structural proteins, unremoved hair during unhairing and natural pigments. The materials used include enzyme, saw dust and ammonium chloride or ammonium sulphate.

2.1.1.4. Pickling

After bating, the bated pelt is treated with salt and acid to bring the skin to the desired pH for either preservation (pH 1-1.5) or tanning (pH 2-2.5). This process is known as pickling. After the pickling operation, the skin is theoretically a purified network of hide protein.

2.1.2. Tanyard Operations

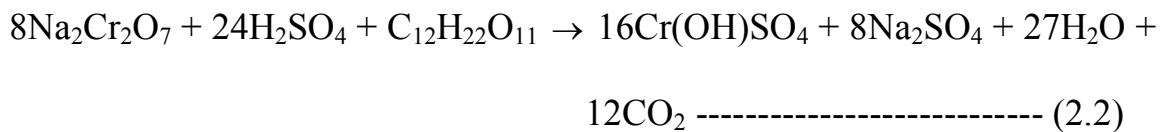
Tanning is the conversion of the pelt to leather. This is carried out by the addition of tanning agents, which could be mineral (e.g. chrome) or vegetable (e.g. bagaruwa). The tanning agent enters in between the leather fibres and does not allow them to stick back when dried. It also has the ability to react with the fibre and cross-link to form large complexes. This is

possible because of the property of the transition element to form complexes and cross link, thereby stabilizing the fibre to withstand high temperature (98-100°C) for chrome tan leather. The cross linking takes place when ageing for about three to four days as a result of the dripping out of the unbound water.

Chromium tanning salts have a valency of +3, are soluble in strong acids but will usually precipitate as chromium hydroxide, or hydrated chromium oxide, at pH above 4. The chrome tanning salts is prepared by treating a solution of sodium dichromate with sulphur dioxide and water to produce a basic chromium sulphate in accordance with the following reaction



A simpler and cheaper method is the reduction of the dichromate as given below;



The process of tanning results in chromium uptake of between 50 to 70%. This implies that over 30% of the chromium is contained in the spent liquor, which can be recycled directly or precipitated for future use in the tannery or mixed with the beamhouse effluent and treated before discharging it into sewer or surface waters. The spent chromium liquor consists of a tanning bath liquor and one or more washes. The chromium concentration of the wash dumps will be significantly lower than that for the bath dump, with each washing becoming more dilute. The tanning bath gave 6260 mg/l of chromium, while the first wash gave 2417 mg/l, (Maire, (1977)). Segregated spent chromium liquor is obtained from the bath after tanning.

2.1.3. Finishing Operation

The finishing operation of leather includes; dyeing, fatliquoring and mechanical processes.

2.1.3.1. Dyeing.

Leather is coloured to improve its appearance, to make it adaptable for fashion, styling and ultimately to increase its value as a commodity. The colour of leather may be derived from processes involving natural and synthetic dyes, pigments, and a combination of pigments and dyes. Dyes suitable for leather colouring may be grouped into anionic and cationic types. Anionic dyes are alkali salts of the dye acid used for leather and

include acid (wool) dyes, direct (cotton) dyes, mordant dyes, metal complex dyes and the pigment (acetate) dyes. Anionic dyes combine with chrome leather and become bound through primary and secondary valence forces. Cationic dyes, however, have little affinity for chrome leather and require a mordant. Thus dyeing with cationic (basic) dyes may be considered as co-precipitation or lake formation.

The selection of the individual dyes is governed by their dyeing behaviour and fastness properties. The dyer will prefer those that dissolve readily in water even at pH values below 3.4, but also yield shades of high fastness to water.

2.1.3.2. Fatliquoring.

This is a process whereby oils are incorporated into leather from an emulsion before the leather is dried. The application of oil in the emulsified form differentiates between fatliquoring and other means of incorporation such as stuffing, currying etc. Oils and grease incorporated into leather are generally classified as leather lubricant.

The incorporated oil influences the degree of cohesion, which takes place during drying. It is also believed that it acts to control the differential shrinkage of grain versus corium of the leather during drying, playing a role in controlling the tightness or break of the leather.

The predominant classes of fatliquors throughout the leather industries include;

1. The mayonnaise – type fatliquor which is an oil in water emulsion where the emulsifier is primarily soap or soap and a protective colloid.
2. Sulphated oil of various types.

2.2. Tannery Effluent

The processing of hides and skins into leather is carried out in an aqueous medium, hence the discharged water from pits, drums or paddles containing several soluble and insoluble constituents constitute the effluent from the tannery. Based on different studies of the material balance in leather production, the processing of one thousand kilogramme (1000 kg) of wet-salted raw hide into chrome – tanned upper or upholstery leather, result in the production of two hundred kilogramme (200 kg) of the products, 30 – 40m³ waste water and considerable amount of solid wastes and by products. The sludge generated by wastewater treatment amount to approximately 350 – 450 kg (at 35% of dry substance) (Buljan et al, (1998)

Materials in tannery effluent may include bits of flesh, hide scraps, hair, blood, manure, earth, salts, soluble proteins, suspended lime, sulphites and sulphides, amines, arsenic, tannins, soda ash, sugars, agents, mineral acids, dyes, and other organic and inorganic compounds (O’Flaherty et al (1978)). The amount of pollutants likely to occur in processing wet – salted hides for chrome shoe upper leather and vegetable tanned leather are given in Table 2.1 (Sharphouse (1983)). These figures quoted are possible averages that may vary with different tanneries, the types of hides or skins processed and the processing technique employed

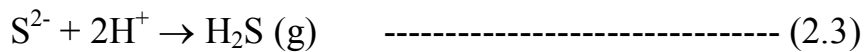
Table 2.1: Amount of Pollutant per Tonne of Raw Wet-Salted Hide for European countries (Sharphouse, (1983))

Pollutants	Average range (kg)	Concentration mg/l
Cl ⁻	160	2500
Total N ₂	10 –40	120 - 250
S ²⁻	7	100 – 160
SO ₄ ²⁻	40	700 (Cr tan)
Alkalinity	750	pH 10
Total Solids	300 – 1000	1000
Suspended Solids	70 – 200	2500 (Cr tan) 1500 (Veg. tan)
Ash in Suspended Solid	60	1000 (Cr. tan) 500 (Veg. tan)
Chrome	4.5	70
Fats		350
BOD	60	900 (Cr tan)
	85	1700 (Veg. tan)
COD	175	2500 (Cr tan) 3000 (Veg. tan)

2.3. Effect of the Pollutants on the Environment

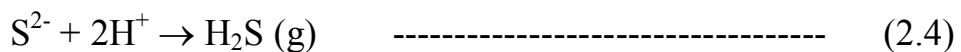
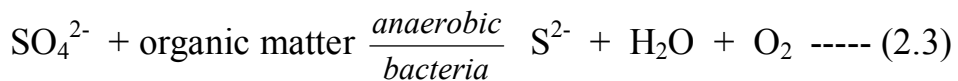
The adverse effects of these pollutants on the environment are explained below.

1. **Chlorides:** These are mainly as salts and have adverse effect on fresh water life and are also harmful to the growth of vegetation. Excess chlorine may form chloroform by reaction with peat. This is a possible cause of the cancer of the gut and bladder (Lee (1991)).
2. **Sulphides:** These produce smell and in acid media liberate poisonous hydrogen sulphide gas, in which one gram per cubic metre (1g/m^3) in air is lethal even after a short exposure.



The gas may also greatly reduce the biological oxygen content of water, which is essential to fresh water life. It also causes corrosion problems in metallic and concrete tanks.

3. **Sulphates:** These are undesirable as they release hydrogen sulphide gas under anaerobic conditions, giving similar effect as in (2) above. The reactions are given below:



4. **Alkalinity:** High pH inhibits many types of plants and animal life and the efficiency of bacterial bed degradation in sewage plant.

5. **Total Suspended Solids:** These may deposit in pipe work etc. causing blockages or may lie as a blanket of mud on river beds inhibiting life there. If remaining in suspension, they give turbidity to the water, impeding the penetration of light for photosynthesis of plants and serve as infrared absorber. Depending on their nature, they may give rise to smells from putrefaction and affect the Biochemical Oxygen Demand and Chemical Oxygen Demand values.
6. **Chrome Oxide:** These include chrome from several sources. Chromium (VI) is known to be carcinogenic and corrosive to tissues. Long-term effects include skin sensitization and kidney damage. Chromium (III), however, is not dangerous and may be tolerated in small quantities. Chromium (III) under alkaline conditions or where they are used for landfills in the presence of manganese (IV) oxide are converted into chromium (VI), (Rutland, (1991), thereby becoming a source of concern.

Maria et al (1999) carried out an investigation into the effects of chromium on workers in the tannery exposed for a period of not less than ten (10) years. The results shows that an average of 222.45 mg/l of chromium was found in the blood of exposed workers as against

2.3 mg/l of chromium for those not exposed. Furthermore, the histopathological data in 55 suspicious cases presents irritation fields of 70% incidence in the exposed group and only 10% in the non-exposed group. This indicates that mucous membrane rhinitis is present when there is exposure to chromium. Skin sensitization of 8.3% was recorded from 131 persons. This buttress the danger posed by chromium to the environment.

7. **Fats:** These may form scum or blockages in pipes and settling tanks. They tend to float on the surface of water, impeding the access of oxygen and light. They may occlude other components, such as hairs or skin detritus, which may then also float on the surface instead of settling to form sediments. Where the fats is held in the form of an emulsion, possibly due to the presence of surfactants, this will impede purification by sedimentation processes and may also cause objectionable foams or froths. Where degreasing processes were employed, the effluent water may also contain quantities of paraffin or other solvents, which may accentuate the floatation problem and cause fire or toxicity hazard or deleterious effects on paintwork or lubricants in the effluent plant.

8. **Biochemical Oxygen Demand:** This is the amount of oxygen required by bacteria for breaking down to simpler substances, the decomposable organic matter present in any water, wastewater or treated effluent, (Ademoroti, 1996). Biological Oxygen Demand (BOD) can be taken as a measure of the concentration of organic matter present in that kind of water. The greater the decomposable matter present, the greater the oxygen demand and the greater the BOD value.
9. **Chemical Oxygen Demand:** This is the measure of the amount of oxygen require for complete oxidation to carbon (IV) oxide and water of organic matter present in a sample of water, wastewater or effluent

2.4. Standards for Tannery Effluent

The tannery effluent as seen earlier is laden with high load of pollutants which are deleterious to man and the environment. Government at Federal State and local levels has the responsibilities to protect its citizens and environments from harmful constituents and set limits for the discharge of such harmful constituents to the environment. Tannery effluent without exception has standards fixed by different nations. Table 2 below gives the standards for Germany, Italy, Kenya, World Health Organization, (WHO)

and Nigeria. These standards are followed by legislation that imposes some penalties in cases of violation.

Table 2:2. Tannery Effluent Discharge Limit. [Buljan and Bosnic (1994) and *FEPA (1991)]

	GERMANY		ITALY		KENYA		WHO		*NIGERIA
	Surface	Sewer	Surface	Sewer	Surface	Sewer	Surface	Sewer	Surface
Chlorides, mg/l		600	1000	1200		3000	1	400	600
Total N ₂ , mg/l	5 – 10	200	10-15	30		100		500	20
Sulphide, mg/l	1	2	1	2			1	10	0.2
Sulphate, mg/l		600	1000	1000		100		1000	500
Alkalinity, pH	6.0-8.5	6.5-10.0	5.5-9.5	5.5-9.5			5-9	6-10	6 - 9
Suspended solids, mg/l	20-25		40-80	200			40	1000	30
Chrome, mg/l	1	2	2	4	1				2
Fats/oil/grease, mg/l	20	250	20	40	trace	100			10
BOD ₅ , mg/l	20-25		40	250	20	450	20	8	50
COD, mg/l	200		160	500					160

Comparison of Table 2.1 with Table 2.2 shows that the pollutants in tannery effluents usually exceed the permissible limit for discharge into surface water and sewer, hence the need for treatment.

2.5. Tannery Effluent Treatment

Tannery waste treatment methods may be physical, chemical or biological in nature, used either alone or in combination. They can be applied to individual fractions of tannery wastes, combined tannery wastes, or tannery wastes combined in various proportions with other industrial and domestic sewage. The waste could be treated completely at a tannery or can be given a preliminary treatment at a tannery and discharged to a municipal sewage system and treated along with domestic sewage (O'Flaherty et al (1978)).

The treatment and disposal of tannery waste can be simplified greatly by simple process of separating the relatively clean wastes from highly contaminated wastes. Special drains and tanks are installed to handle the more contaminated effluent, normally from the limeyard and tanyard, which may comprise only 25% of the total effluent, the remainder being wash waters, etc, which are relatively clean and enter the discharge system by-passing those of high contamination. The merit of segregating the effluent

before treatment includes effective reduction in equipment size, increase in treatment efficiency and operational flexibility of the treatment facility. Furthermore, the less contaminated water can be re-used or they can be mixed with treated effluent to decrease the concentration of pollutants not completely removed by treatment. Investigators at State College of Michigan found that such a separation of wastes at one tannery reduced quantities of wastes to be treated from 757m³ (200 000 gallons) to 160m³ (80 000 gallons) per day (O'Flaherty et al, (1978)).

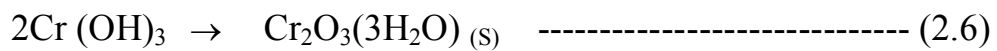
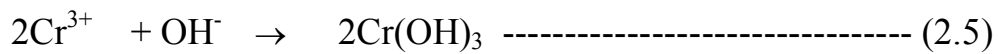
Wastewater treatment can generally be divided into four classes viz;

1. Pre-treatment: This process can be sub-divided into equalization, neutralization, grease and oil removal and the removal of toxic substances.
2. Primary treatment: This involves screens, grit chambers, gravity sedimentation and chemical precipitation.
3. Secondary treatment: This is made up of biological reactors, activated sludge, lagoons, trickling filters, biological fluidized beds etc.
4. Physical – Chemical treatment: This comprises of adsorption, ion exchange, chemical oxidation and membrane processes (Perry and Green (1998)).

Individual units and or combination of units from the different classes can be used depending on the type of wastewater to be treated and the type of treatment envisaged.

2.5.1. First stage of treatment:

The traditional method used for treating tannery effluent was to lead all process drains into one common mixing tank. Here some degree of neutralization of the lime liquors takes place by acid deliming pickle or tan liquors. Some of these process liquors react with each other resulting in the formation of insoluble precipitates, which form as a sediment in tanks. For instance lime could precipitate chromium oxide according to equations 2.5 and 2.6.



The time needed for such sedimentation varies, but it is often held at a minimum of six hours and the tank should be large enough to hold six hours discharge of effluent at maximum rate of discharge.

The proposed process for the CHELTECH (Zaria) effluent treatment is made of two tanks, one for beamhouse and the other for the tanyard effluent. The current process requires that both effluents be mixed, thereby conforming to the traditional method used. The effluent is collected and screened through a 1.60 mm mesh. This removes hair, trimmings, fleshings or wool, thereby avoiding blockage in the system. In this first stage about 80% of insoluble materials are removed from the effluent. Further 30 – 50%

of organic matter according to BOD₅ and about 5% of the sulphide present is removed (Halamek et al, (1971)). If not for the presence of sulphide and chromium in high amount, such effluent after sedimentation falls into the category of that which may be accepted into urban sewage at a cost dependent upon quality and purity.

2.5.2. Second stage of treatment:

The second stage of treatment is Chemical and or Biological treatment. Chemical treatment is basically precipitation of soluble proteinous impurities by coagulation with Iron (II) Sulphate in doses of 1 to 2g of Iron (II) sulphate heptahydrate per litre of water. In Biological treatment, natural methods are used such as biological ponds, soil filtration, and irrigation of soil. Artificial method used in biological treatment includes aeration of water in biological filters or treatment with activated sludge.

The above-mentioned method of treatment is able to reduce the content of harmful matters, determined according to BOD₅, by 60 – 70% with chemical treatment and by up to 90% with biological treatment (Halamek (1971)).

2.5.3. Sulphide removal

The high sulphide content, due to its high BOD rating, corrosive effects and liberation of poisonous hydrogen sulphide gas in acid media, is undesirable in public sewers or surface water.

Relative distribution of sulphides in water is closely related by the equation.

$$H_2S/T = [(H^+)/K_1]/[2 + (H^+)/K_1] \text{ ----- (2.7)}$$

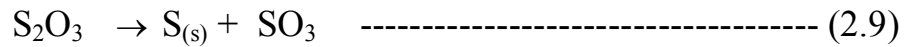
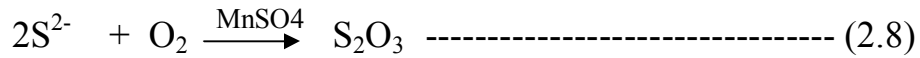
Where T is the total dissolved sulphide (mg/l)

$$K_1 \simeq 10^{-7}$$

The effect of the second dissociation constant is negligible at the pH values of most water. It therefore, follows that low pH favours hydrogen sulphide removal (Fair et al, (1968)).

2.5.3.1. Catalytic oxidation of tannery effluent:

The screened tannery effluent is subjected to catalytic oxidation using 0.1g of Manganese sulphate per litre with aeration. The sulphide reacts with oxygen to give sulphur as shown by the equations below:



Analysis shows that after a period of approximately four hours, the sulphide is decreased to almost zero. This reaction has been studied by a number of workers and is in practical uses in many tanneries in the United States (Thorstensen, (1976)). The sulphur obtained could be sold or used to prepare sodium sulphide, which can be used in the tannery.

2.5.3.2. Hydrogen sulphide release process:

There are several processes developed to remove the sulphide as hydrogen sulphide gas. Two of such processes shall be discussed below.

i. Sulphide recovery:

In this process the beamhouse waste are sent to the classifier for settling. Chromium tanning waste are collected and precipitated before recycling. The overflow from the classifier being at a high pH (10 – 12), contains some quantities of lime and suspended matter. The clarified overflow contains sulphides.

The clarified overflow is acidified with sulphuric acid in the acid scrubber where it flows from plate to plate from the top down to the bottom, reducing the pH to less than 5, thereby releasing the sulphide as hydrogen sulphide gas. There is a counterflow of air from the column to carry away the hydrogen sulphide gas generated into the secondary scrubbing column, where a spray of sodium hydroxide flows over the packed column, which scrubs the hydrogen sulphide gas as shown by the equations below:

Acid scrubber



Alkaline scrubber

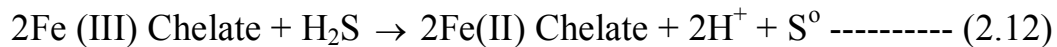


The waste at pH of about 5.5 is then adjusted to between 6.0 and 9.0 and discharged to municipal sewer system. The final effluent contains no chromium, no sulphide and only a small amount of suspended solids and BOD. The sulphide accumulates in the alkaline tank and is recycled for used in the beamhouse (Thorstensen (1993)).

ii. Sulphur recovery

The first step in this process is an anaerobic biological treatment using an upflow anaerobic sludge blanket (UASB) or an expanded granular sludge blanket (EGSB) reactor. In this step, a large part of the dissolved oxygen (DO) is eliminated and converted into biogas, a mixture of methane and carbon dioxide gas. In addition, all sulphur compounds (e.g. sulphate, sulphites, organosulphur) are converted into sulphide, which can accumulate to high levels.

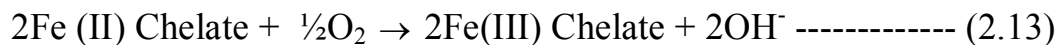
The reactor liquor is passed through a stripper in which the sulphide is transferred as hydrogen sulphide to a stripping gas. The stripping gas is drawn from the produced biogas. Because of the stripping process, the sulphide concentration will decrease dramatically. After passing the stripper, the liquor is returned to the anaerobic reactor. The hydrogen sulphide bearing gas from the stripper is transported to an absorber in which the hydrogen sulphide is absorbed in a solution containing Iron (III) chelate (redox liquor). The chelate is a complexing agent such as EDTA. The reaction is given below:



The clean gas having a low hydrogen sulphide concentration is returned to the stripper again to absorb another load of hydrogen sulphide.

The net amount of gas produced leaves the system as a clean biogas, which can be used in gas motors.

The liquor from the absorber is transported to a settler in which sulphur is separated from the supernatant. The sulphur slurry can be further processed to make it fit for use as raw material in the chemical industry. The supernatant containing iron (II) chelate is regenerated by aeration according to the equation below:



The dissolved iron (III) chelate is recycled to the absorber. The result obtained shows that 70% of COD and more than 90% of sulphur compounds are removed. The removed sulphate and sulphite are recovered as elemental sulphur with 30 – 60% (w/w) slurry and the purity greater than 99% w/w, which can be used in sulphuric acid factories (van Groenestijn (1999)).

2.5.4 Chrome recovery processes

The objective of chrome management is not only to avoid pollution load due to chromium, but also to improve the efficiency of the biological systems of composite wastewater at large, since the chromium sulphate bearing effluent have a deleterious influence on the efficiency of biological system of treatment. The solution concentrations of metallic species (Me^{Z+}) kmol/m^3 , in this case chromium, in an aqueous medium with hydroxide concentrations (OH^-) kmol/m^3 , is defined by the solubility product K_s as

$$K_s = (\text{Me}^{Z+}) (\text{OH}^-)^Z \text{-----} \quad (2.14)$$

Thus

$$\text{Log} (\text{Me}^{Z+}) = \text{Log} K_s - z\text{Log} (\text{OH}^-) \text{-----} \quad (2.15)$$

or

$$\text{Log} (\text{Me}^{Z+}) = \text{Log} K_s + z\text{pOH} \text{-----} \quad (2.16)$$

Where

$$\text{pOH} = - \text{Log}(\text{OH}^-)$$

In the presence of other ions, the activity (a) replaces the metal ion concentration in equation (2.14) and (2.15). Thus

$$\begin{aligned} \text{Log} (a) &= \text{Log} (f \text{Me}^{Z+}) \\ &= z\text{pOH} - (- \text{Log}K_s) \text{-----} \end{aligned} \quad (2.17)$$

where f is the activity coefficient for metal ions, dimensionless. Hence,

$$\text{Log} (f \text{Me}^{Z+}) = z\text{pOH} - \text{p}K_s \text{-----} \quad (2.18)$$

f is calculated from the ionic strength (I) of the solution in kmol/m^3 , and the charge on the metal ion z , by the expression below,

$$- \text{Log}f = \frac{0.5z^2I}{1 + I} \text{-----} \quad (2.19)$$

The removal of chromium may be by direct recycling, recycling by precipitation with an alkali or by co-precipitation of the chromium with the beamhouse waste.

1. Direct reuse of chromium liquors

In the direct recycling process, the spent chromium liquor with a pH of 3.5 – 4, is fortified with salts and acids to drop the pH to less than 2 before it is reused. There is, however, a certain build up of salts in the spent chromium liquor as it is recycled and this is a function of the liquor ratios

used during tannage. In the conventional recycling process two methods are used viz;

- i. Pickling to a pH of 4.0 followed by a pre-treatment with ethanolamine prior to tanning with 5 – 6% basic chromium salt.
- ii. Combination of aluminum based synthan and basic chromium salt.

In both processes, the discharge of chromium in the spent liquor is low, about 1.0 mg/l. Therefore, the spent chromium liquor can be recycled as pickle liquor for the subsequent batch without any negative consequence.

2. **Chromium recycling by precipitation:**

This process involves precipitation of chromium with an alkali like magnesium oxide (soda ash and sodium hydroxide were used in “the seal tanning system” (Thorstensen, (1993)) and the precipitated chromium hydroxide is allowed to settle down. These reactions are represented by equations (2.5) and (2.6).

The clear supernatant liquor is then removed by siphoning and discharged. The precipitated chromium slurry is redissolved in a calculated amount of sulphuric acid to adjust the basicity to a level of 33%. The recovered chromium can be reused along with fresh chromium in proportion of 1:2. A result obtained for using 725.75 kg of chromium per day without recycling results in dumping 145.15 kg, while with recycling 5.44 kg was dumped (Thorstensen (1976)). This explains why this process is in vogue and shall be used in this work.

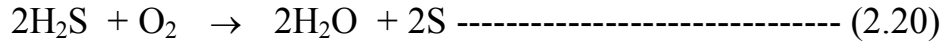
2.5.5 Ferrous sulphate and aluminum sulphate treatment processes

This is considered the last chemical treatment of tannery effluent before biological treatment or discharge to public sewers. In some cases aluminum sulphate is used. These treatments are most often carried out in the presence of lime or at high pH, i.e. above 9.

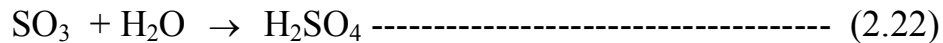
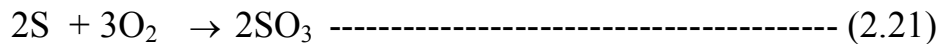
2.5.5.1. Lime – Ferrous sulphate oxidation system

This consists of a balancing pit, which receives mixed effluent, i.e. tannery and other related manufacturing effluent. The balancing pit is made to maintain an inflow for twenty-four hours, and the plant capacity must be

1.4 – 2 times the daily effluent volume. Compressed air is then mixed thoroughly with the effluent by passing them through a stationary partitioned screw pipe into the primary setting tank. The air provides the necessary oxygen and simultaneously agitates the liquor. The aeration causes a rise in pH and hence affects the ionization equilibria of hydrogen sulphide, thereby stepping up the hydrogen sulphide ion and sulphide ion concentration. In addition, the oxygen in the air reacts, with the hydrogen sulphide to form sulphur, according to the following equation:



The sulphur thus formed can further be oxidized to form sulphate, thus



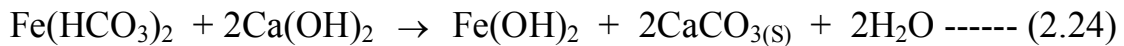
The reaction given by equation 2.20 helps to remove residual sulphide where it had not been precipitated in previous stages.

Lime is then added to control the pH, so as to ensure that all subsequent processes are carried out at a constant pH and also enhance the removal of sulphur and chrome. The sludge thus formed is allowed to settle, removed and dewatered.

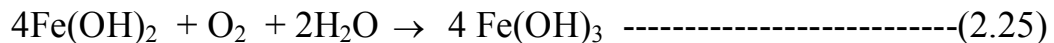
The supernatant flows into the precipitation unit where it is dosed with ferrous sulphate and further aeration to complete the chemical treatment e.g.



Reaction with lime.



Reaction with oxygen.



The insoluble ferric hydroxide is formed as a bulky, gelatinous floc. During this process, inorganic and organic substances, turbidity, colour, harmful bacterial organisms, taste and odour – producing substances and phosphates, which serve as nutrients for the growth of algae, are removed. During flocculation process, the colloidal material come together and become incorporated into masses that can be readily precipitated [Tchobanoglous and Burton, (1991)]. The optimum pH for the removal of negative colloids falls in the range of 4.0 and 6.0. Consequently, both iron

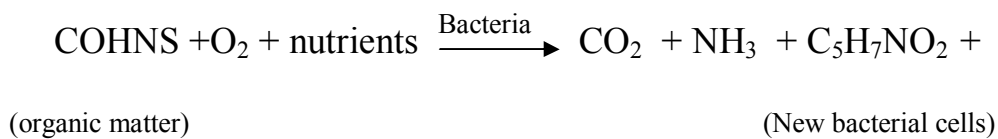
and aluminum ions are completely precipitated at pH levels as low as 5.0 and very little Fe^{3+} and Al^{3+} remain in coagulated water. It was also discovered that at pH below 4.0, the OH^- is insufficient to precipitate Fe^{3+} completely so that $\text{Fe}(\text{OH})^{2+}$ and $\text{Fe}(\text{OH})_2^+$ occur.

For the same reason Al^{3+} is incompletely precipitated at pH levels below 5.0 so that $\text{Al}(\text{OH})^{2+}$ and $\text{Al}(\text{OH})_2^+$ occur. These facts indicate why it is essential to have residual alkalinity during chemical coagulation. The residual alkalinity serves to buffer the system at pH level above 5.0 for Al^{3+} and 4.0 for Fe^{3+} to ensure complete precipitation of the coagulating ions. Slaked lime is used in slurry form to serve as floc conditioner, alkalinity adjuster and water softener when mixed with Al^{3+} and Fe^{3+} . Under alkaline conditions [Ademoroti (1996)*].



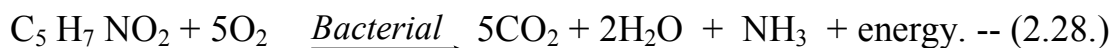
The effluent thus obtained undergoes biological treatment with activated sludge and oxygen added.

Oxidation and synthesis:



other end products ----- (2.27)

Endogenous respiration:



Although the endogenous respiration reaction result in relatively simple end product and energy, stable organic end products are also formed. From equation 2.28, if all the cells can be oxidized completely, the ultimate BOD of the cells is equal to 1.42 times the concentration of the cells.

The treated effluent then passes to the secondary settling unit where auxiliaries are added to accelerate sedimentation of the mixed sludge. The settle sludge is then removed and dewatered. Analysis of the effluent is given in Table 2.3.

Table 2:3 Analysis of the treated effluent from lime – Ferrous sulphate oxidation system (Wachsmann, 1978).

Parameters	Amount mg/l	Percentage (%) removed
Sulphide	0.1	
pH	7.2	
Iron	1.2	
Chromium	0.015	
BOD	17	93%
COD	51	80%

2.5.5.2 Idronova – Hüni Process

This is an integrated treatment process comprising sulphide recovery, chromium recovery, chemical coagulation with aluminum sulphate and biological treatment using trickling filters. The beamhouse effluent is treated to remove sulphide, while the tanyard effluent is treated to remove chromium. Both effluents are then given chemical treatment using aluminum sulphate and lime followed by biological treatment using trickling filters. The watery sludge from the filters is further treated with polyelectrolyte to improve flocculation and to produce a sludge having up to 30% dry matter. The analysis of the results obtained by this treatment process is given in Table 2.4.

Table 2 :4 Results obtained with Idronova Combine treatment process for complete hide tannery (Wachsmann, 1978).

Contaminants	Before	After Chemical		After biological	
	Treatment	Treatment	(%)	Treatment	(%)
pH	8.9	6.7		6.7	
Chloride (mg/l)	1230	1230		1230	
Sulphide (mg/l)	175	2	98.9	0.5	99.9
Suspended solids (mg/l)	1860	50	97.3	16	99.1
Sediments (ml/l)	135	0.1	99.9	-	100
Iron (mg/l)	-	0.5		0.5	
Chromium(III) (mg/l)	78	1	98.7	1	98.7
Chromium(VI) (mg/l)	0.1	0.1		0.1	
Phenols (mg/l)	15	0.5	96.7	0.5	96.7
Oil & grease (mg/l)	32	8	75.0	5	84.4
BOD ₅ (mg/l)	1780	210	88.2	35	98
COD (mg/l)	2800	550	80.4	270	90.3

2.6. Treatment Process at CHELTECH, Zaria

A two-stream treatment scheme was adopted for the treatment of CHELTECH tannery effluent. These are:

1. The stream without chromium

2. The stream containing chromium

2.6.1. The stream without chromium

The stream without chromium carries the Beamhouse effluent, which is alkaline, due to the liming and unhairing process that were carried out on the hide/skin. The stream leads the effluent to a collection tank. The effluent is treated in this tank to remove sulphide. This is carried out by dosing the effluent with a calculated amount of manganese sulphate catalyst and aerating for a specified time. This is then allowed to settle overnight. The supernatant is then pumped to the chromium containing effluent. The sludge is then scooped and allowed to dry before sending it for landfill.

2.6.2. The stream containing chromium

The stream containing chromium comes from the tanyard, which is acidic, due to the pickling and tanning processes carried out on the pelt. The effluent also contains spent dyes and fatliquor. This leads to two pits in succession. The effluent is led to pit 1. The volume of this effluent is small compared to the effluent from the beamhouse.

The effluent coming from the tank enters pit 1 to mix with the tanyard effluent thus raising its pH to value above 9. The combined effluent is

further dosed with ferrous sulphate or aluminum sulphate and agitated for a given time. This will effect the precipitation of chromium tannins, spent dyes and spent fatliquor. This is then allowed to settle and the supernatant is transferred to pit 2. The sludge is then removed, dried, and sent for landfills. It could also be joined with the sludge from the beamhouse effluent tank before disposal. The treated effluent in pit 2 with high pH, about 10 – 12, will have its pH adjusted to about 6 – 9 and then sent to sewers.

This process has its shortcoming because the sludge precipitated or digested before landfills contain a large amount of chromium. This chromium though in the form of chromium (III), is liable to conversion into chromium (VI) under alkaline conditions or in the presence of manganese (IV) oxide, which is toxic and carcinogenic. Chromium (VI) can be taken up by plants or washed into streams and rivers, and is lethal to both man and animals. Furthermore, this does not give room for the recovery of chromium either by direct recycling or recycling by precipitation. This, therefore, shows the inefficient use of chromium, resulting in its wastage.

2.6.3. Current practice

The treatment processes at CHELTECH is stalled due to poor funding. The current practice therefore, is the channeling of the effluent from the Beamhouse and tanyard directly to pit 1. Here precipitation of the

chromium, tannins, spent dyes and fatliquor takes place. This is also followed by the release of hydrogen sulphide gas to the atmosphere.

These processes are continued until pit 1 is filled up. It then drains into the second pit. This is continued until both pits are filled. The effluents from both pits are then pumped into the gutter and the bottom of the tank scooped to remove settled matter.

2.6.4. Material balance and chromium analysis of CHELTECH's tannery.

CHELTECH's, Zaria tannery is designed to process 250 kg/day of hides/skin. Material balance per annum based on established processes using twenty (20) working days per month is given in Figure 2.1.

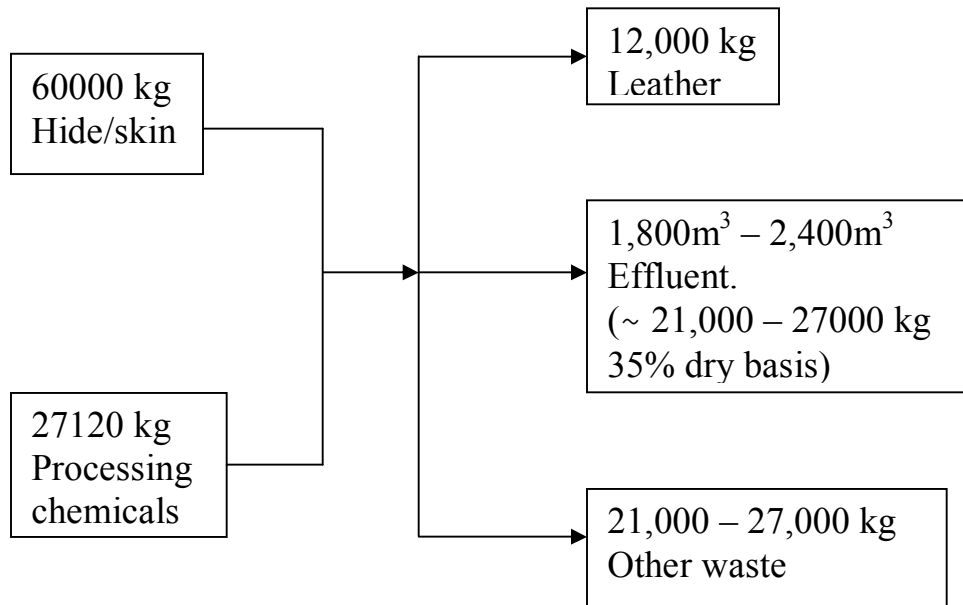


Figure 2.1 Material balance for CHELTECH's tannery per annum

The tannery will require 3,600 kg of chromium salts costing N900,000:00 at N250:00 per kg. Where 70% of chromium salts uptake occurs, chromium that is sent to the drain will be equal to 1080 kg amounting to a loss of N270,000:00. This will amount to a great loss economically and a danger to the environment; hence, treatment of the effluent and recovery of this chromium cannot be overemphasized.

4.	Metler Balance	Model P 1200	Metler Instrument Ltd, Switzerland
5.	Sieve 1.6 mm	Model 5446 -64	
6.	Oven	0 – 200 °C	Gallenkamp, England.
7.	Steam bath	No. 9A 395	Gallenkamp, England
8.	Laboratory Hot Plate/Stirrer	Model PC 351	Corning Glass Works, N.Y.
9.	Full range Indicator paper.	pH (1 –14)	BBR Chemocraft
10.	pH meter.	Kent EIL 7055	
11.	Flask Shaker	Cat. No. 5D 110	Gallenkamp, England.

3.3. Experimental Procedure

3.3.1. Sample collection and preparation.

1. Sample collection. Two sets of samples were collected. The first sample was a combination of effluent from beamhouse, tanyard and finishing operations, henceforth referred to as sample 1 (mixed effluent). The second sample (sample 2) was spent chromium liquor obtained after chromium tanning of the pelt in the tanyard.

2. Sample preparation and analysis.
 - i. Sieving. Both samples were sieved using 1.6 mm sieve size and were analysed for total solids, suspended solids and dissolved solids.
 - ii. Filtration. Both samples were filtered using Whatman No. 1 filter paper. Sample 1 was then analysed for chromium, BOD, COD, nitrate grease, sulphate and chloride. While sample 2 was analysed for only chromium.

Treatment with different concentrations of magnesium oxide and different contacting time.

1. Treatment for sample 1. Six sets of the samples were taken per run and dosed with different concentrations of MgO. These were agitated using the shaker at 8 revolutions per second for a given time. This procedure was repeated for other different times. The resultant mixture obtained were filtered and analysed for pH. This was then used to calculate the percentage of chromium removed, according to equations 2.14 and 2.15.
2. Treatment for sample 2.
 - i. Treatment with various concentrations of MgO. Six sets of samples were prepared with different concentrations of MgO. These were then

agitated using the shaker at 8 revolutions per second for 30 minutes. The resultant was then filtered and analysed using Atomic Absorption Spectrophotometer (AAS).

ii. Treatment with a chosen concentration of MgO for different contacting time. Samples were prepared, dosed with the chosen concentration of MgO obtained in 3.3.2.2. (i) above and agitated using the shaker at 8 revolutions per second for different contacting time. The resultant mixture was then filtered and analysed using Atomic Absorption Spectrophotometer (AAS).

4.3. Treatment with a chosen concentration of MgO, followed by treatment with ferrous sulphate for Sample 1. Sample 1 was dosed with a given amount of MgO and agitated for a given time (chosen time). This was then dosed with 1500 mg/l ferrous sulphate and agitated using the shaker at 8 revolutions per second for 30 minutes. The resultant mixture was filtered and analysed for nitrate, COD and BOD.

4.0. RESULTS AND DISCUSSION

4.1. Wastewater Characterization

The results of analysis of samples 1 and 2 are given in Table 4.1.

Table 4:1 Contaminants in CHELTECH Tannery Effluent - sample 1 and sample 2

S/No	Contaminants	Sample 1	Sample 2
1	Chloride (mg/l)	57.98	NA
2	Nitrate (mg/l)	95	NA
3	Sulphate (mg/l)	105	NA
4	pH	7 - 9	3
5	Total Solids (mg/l)	15050	98264
6	Suspended Solids (mg/l)	900	922
7	Dissolved Solids (mg/l)	14150	97342
8	Grease	7950	NA
9	Chromium (mg/l)	29.86	7020
10	COD (mg/l)	4200	NA
11	BOD (mg/l)	1600	NA

NA – Not analysed because the focus was on the chromium in the tanyard effluent.

The results obtained for both samples show that the Total Solids, Suspended Solids, Dissolved Solids, grease, chromium, BOD and COD were higher than the statutory effluent discharge limits for tannery effluent presented in Table 2.2. The values of TS, DS and chromium for sample 1 were generally lower than that for sample 2. This is expected due to the natural law of dilution. The large volumetric effluent from the beamhouse with zero concentration of chromium when combined with the tanyard effluent with high chromium concentration literally produced mixed effluent having bulk chromium concentration lower than that from the tanyard effluent. The high pH of sample 1 is equally valid because it naturally favours the precipitation of most metal ions and clarification of organic suspensions, thereby giving lower values of TS, DS and chromium for sample 1. This pH results are in agreement with Ademoroti's (1996)* observation on effect of lime on sewage loaded with heavy metals.

The total solids in Samples 1 and 2 of 15050 mg/l and 98264 mg/l respectively are higher than common averages of 1000 mg/l elsewhere (Sharphouse, 1983). Nevertheless, that of sample 1 was within the range reported for contemporary Nigerian Tanneries (4011 – 19496 mg/l) (Lawal and Singh, 1983).

The amount of chlorides, nitrate, sulphate, chromium, COD and BOD obtained for sample 1 are lower than those reported by Lawal and Singh (1983) and Sharphouse, (1983). This could likely be due to the precipitation of some of the contaminants in the effluent due to the mixing of the beamhouse effluent and the tanyard effluent. Comparing the amount of

chromium in sample 1 and 2, the high value obtained for sample 2 (7020 mg/l) is a pointer that when the samples are segregated the amount of chromium will be very high giving the tendency for higher recovery. The value in sample 2 is comparable to 6260 mg/l obtained by Maire, (1977) for a similar process.

4.2. Chromium Removal

4.2.1. Dosage with various amounts of magnesium oxide for different contacting time for sample 1.

The analysis of the effluent after dosing with various amounts of magnesium oxide for different contacting time for sample 1 is shown in Figure. 4.1.

The result obtained shows a marked increase in chromium ion removed with increase in contact time from 15 to 120 minutes as MgO concentrations were increased from 10 to 60 mg/l. The use of as low as 20mg/l of MgO after 120 minutes was able to effect chromium removal of above 96.8%. The highest chromium ion removal of 99.8% was recorded when 40 mg/l to 60mg/l of MgO were used for contacting time of 90 to 120 minutes (Table I.3, Appendix I). The high values of chromium removal could be as a result of the initial pH of sample 1 (7), hence little MgO was

enough to raise its pH thereby effecting the removal obtained. This results compare favourably with that obtained by Idronova Hüni treatment system of 98.7% chromium removal.

The final chromium concentration of the treated effluent (0.06 mg/l), shown in Table I.1 in Appendix I, compares favourable with that obtained by the Lime – Ferrous oxidation process of 0.015 mg/l, (Wachsmann, (1978) and is within the recommended limit for discharge into sewers and surface waters, (Buljan and Bosnic, (1994). Nevertheless, the presence of lime in the precipitated chrome from sample 1 renders the recovered chrome non reusable due to the likelihood of gypsum formation when redissolved in sulphuric acid.

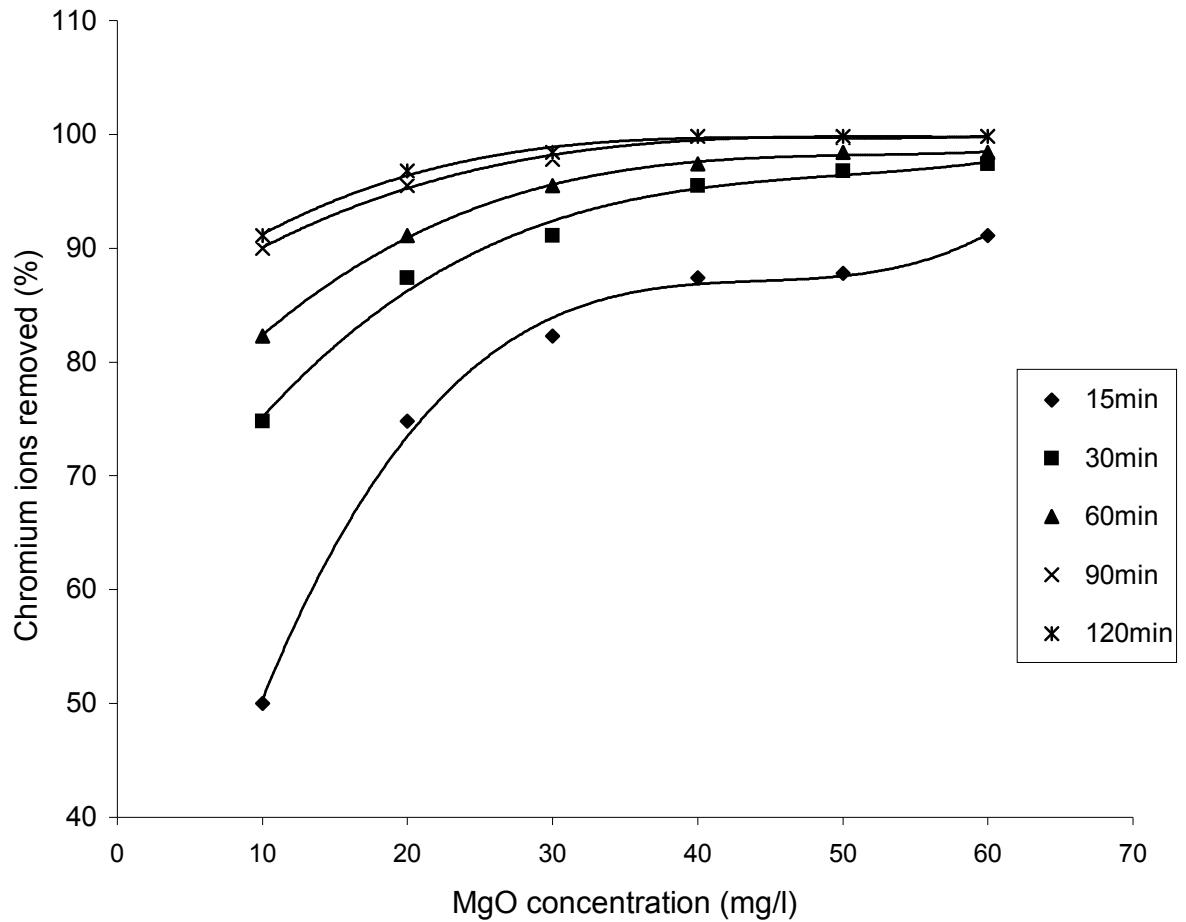


Figure 4.1 Effects of MgO concentration and contacting time on chromium ions removal from tannery effluent for sample 1.

4.2.2. Treatment of sample 2 with different concentration of MgO for 30 minutes.

The result in Figure 4.2 shows a sharp increase in the chromium ion removal from 18% to 80% when the concentrations of MgO were increased from 50 to 400 mg/l. The high concentrations of the chromium ion and the acidic nature of the effluent informed the high

amount of MgO used as compared to that used for sample 1. For instance to obtain 85% chromium ion removal, 14 mg/l of MgO was used on sample 1 while 700 mg/l of MgO was used on sample 2.

Increase for MgO used results in a corresponding increase in the chromium (III) oxide trihydrate precipitated, as shown in Table II.1 in the appendix. This probably led to mass transfer problem that gives rise to high equilibrium chromium ion concentration in the solution. Hence, further increase of MgO from 400 mg/l to 900 mg/l offered only 6% additional chromium ion removal. The 86% chromium removal, which is equivalent to 6037.8 mg of chromium ion from each litre of the treated effluent, could be regarded as substantial. However, the relatively high value of 982.8 mg/l (Table II. 1, Appendix II) of chromium ion in the outlet stream suggest the need to adopt multiple stage treatment in future investigations to reduce the above mass transfer limitations. This may result in further reduction in the final effluent chromium to an acceptable value.

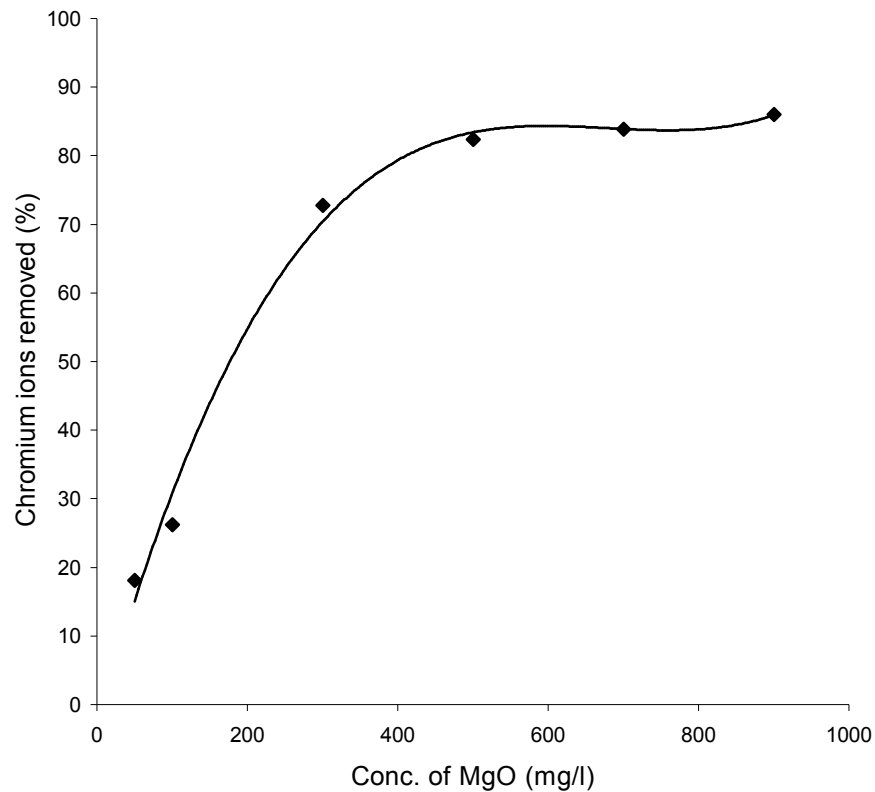


Figure 4.2. Treatment of sample 2 with different concentrations of MgO.

4.2.3. Treatment with 400 mg/l of MgO for different contacting time.

The result in Figure 4.3 showed chromium ion removal of 81% at 30 minutes rising to 89.3% at 75 minutes. The values compared favourably to that of Bayer (1986) who reported 97.1% chromium removal after 120 minutes contacting time.

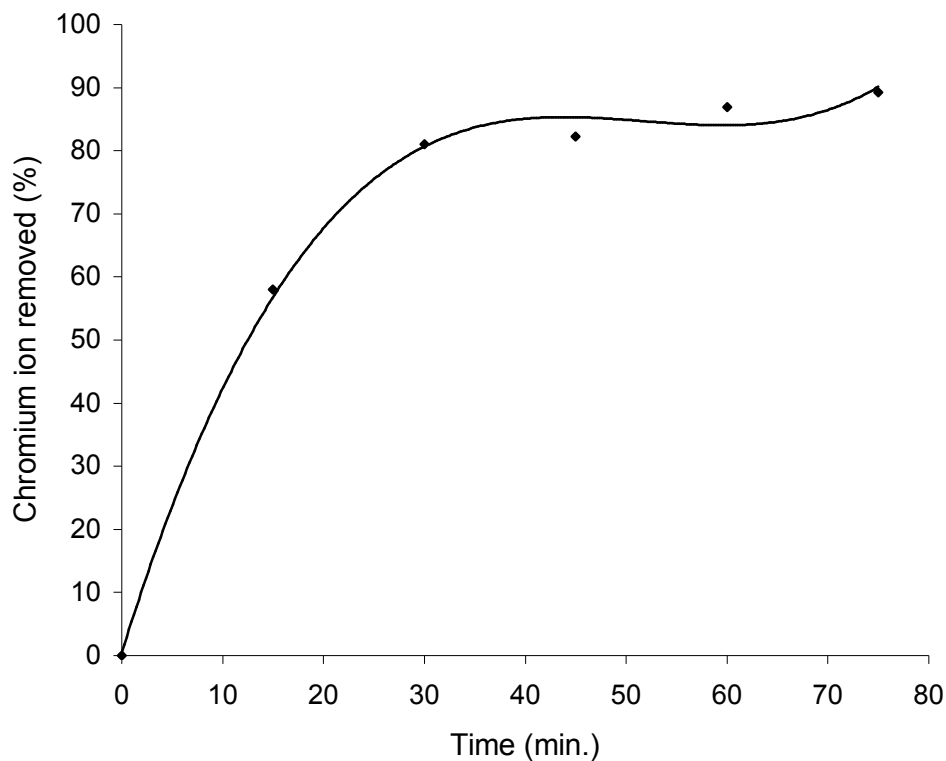


Figure 4.3. Typical effect of time on chromium removal using 400 mg/l MgO for sample 2

Beecroft and Ahmed, (1987) using slaked lime and a combination lime and alum (cheaper material input) in treating an automobile effluent reported 85% chromium removal, which compare favourably with the results obtained using MgO. However, since one of the aims of the present work is to obtain chromium that could be reused in the tannery, the presence of calcium in the effluent due to the liming process as mentioned above is a set back. This is because the conventional method of reusage requires the dissolution of the precipitated metal ions in concentrated sulphuric acid. The

For chromium obtained from the latter process, this will result in gypsum formation as a by-product. Gypsum is known to impart hardness to leather, which is undesirable. Similarly, chromium precipitated by sodium hydroxide are extremely difficult to redissolved after ageing for three weeks. On the other hand, precipitates using MgO are easily redissolved, (Bayer, 1986). These informed the choice of MgO for this work.

4.3. Treatment with MgO followed by FeSO₄

The result obtained is shown in Table 5.2 when treatment of the mixed effluent with MgO was followed by FeSO₄. Nitrate was reduced by 85%, implying that 14 mg/l was left in the final effluent. This value is within the recommended limit for discharge into surface water, (Buljan and Bosnic, 1994).

The percentage COD reduction of 61.9% obtained was lower than that obtained by Idronova Hüni and Lime – Ferrous sulphate oxidation system of 80.4% and 80% respectively. The COD value obtained was above the conventional recommended limit for discharge into surface waters and sewers, (Buljan and Bosnic, 1994).

The BOD was reduced by 76.4% which is lower than that obtained by Idronova Hüni and Lime – Ferrous sulphate oxidation system of 88.2% and

93% respectively. The value of the BOD obtained was above the recommended limit for discharge into surface waters and sewers, (Buljan and Bosnic, 1994). This implied that this method was not adequate in removing the organic degradable materials present in the effluent.

Table 4.2. Dosage with MgO followed by FeSO₄ without aeration

Contaminants	Before treatment	After treatment	
	(mg/l)	(mg/l)	% removal
Nitrate	95	14	85.3
COD	4200	1600	61.9
BOD	1400	330	76.4

Chapter 5.

5.0. CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

Based on the results obtained the following conclusion are made:

1. CHELTECH, Zaria tannery wastewater contains contaminants above the recommended limit for discharge into public waters and sewers.
2. The mixed effluent when treated with 10 to 60 mg/l of MgO for contacting time of 15 to 120 minutes recorded above 40% chromium ion removal.
3. The chromium ion removal of 99.8% was obtained for mixed effluent using 40 mg/l of MgO after 90 minutes.
4. The treated mixed effluent recorded the lowest chromium ion concentration of 0.06 mg/l, which is within the recommended limit of discharge into sewers and surface waters.

5. Treatment of sample 2 for 30 minutes recorded 18 to 86% chromium removal when 50 to 900 mg/l of MgO were used. This was able to remove 6037 mg/l of chromium ions.
6. Treatment of sample 2 with 400 mg/l MgO for different contacting time to a maximum of 75 minutes gave the highest chromium removal of 89.3%.
7. Treated effluent of sample 2 contains effluent above the recommended limit for discharge into sewers and surface waters.
8. Treatment of sample 1 with 20 mg/l MgO followed by 1500 mg/l FeSO_4 gave the following results:-
 - i. 85% of nitrate removal
 - ii. 61.9% COD removal
 - iii. 76.4% BOD_5 removal

5.2. Recommendations

1. The performance of the chromium removed from the effluent should be studied to ascertain its potency in tanning.
2. CHELTECH, Zaria should encourage further research on the various processes of effluent treatment with the view of designing a pilot treatment plant that can also be useful for bigger tanneries.

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APPENDICES

Appendix I. Treatment of sample 1

Table I.1 Amount of chromium in treated effluent after treatment with different concentrations of MgO for different contacting time.

MgO (mg/l) \ Time (min)	10 (mg/l)	20 (mg/l)	30 (mg/l)	40 (mg/l)	50 (mg/l)	60 (mg/l)
15	14.93	7.52	5.86	3.76	3.64	2.66
30	7.52	3.76	2.66	1.34	0.96	0.78
60	5.86	2.66	1.34	0.78	0.48	0.48
90	2.99	1.34	0.66	0.06	0.08	0.06
120	2.66	0.96	0.48	0.06	0.06	0.06

Table I.2 Amount of chromium removed using different concentrations of MgO for different contacting time

MgO (mg/l) \ Time (min)	10 (mg/l)	20 (mg/l)	30 (mg/l)	40 (mg/l)	50 (mg/l)	60 (mg/l)
15	14.93	22.34	24.57	26.10	26.22	27.20
30	22.34	26.10	27.20	28.52	28.90	29.08
60	24.57	27.20	28.52	29.08	29.38	29.38
90	26.87	28.52	29.20	29.80	29.77	29.80
120	27.20	28.90	29.38	29.80	29.80	29.80

Table I.3 Percentage of chromium removed using different concentrations of MgO for different contacting time

MgO (mg/l) \ Time (min)	10 (mg/l)	20 (mg/l)	30 (mg/l)	40 (mg/l)	50 (mg/l)	60 (mg/l)
15	50.0	74.8	82.3	87.4	87.8	91.1
30	74.8	87.4	91.1	95.5	96.8	97.4
60	82.3	91.1	95.5	97.4	98.4	98.4
90	90.0	95.5	97.8	99.8	99.7	99.8
120	91.1	96.8	98.4	99.8	99.8	99.8

Appendix II.**Treatment of sample 2**

Table II. 1. Effect of treating sample 2 with different concentrations of MgO for contacting time of 30 minutes.

Amount of MgO used (mg/l)	50	100	300	500	700	900
Cr in treated effluent (mg/l)	5749.38	5180.76	1909.44	1235.52	1130.22	982.80
Amount of Cr removed.(mg/l)	1270.62	1839.24	5110.56	5784.48	5889.78	6037.20
% of Cr removed (%)	18.1	26.2	72.8	82.4	83.9	86.0

Table II. 2. Effect of treating sample 2 with 400 mg/l of MgO for different contacting time.

Time (min)	0	15	30	45	60	75
Cr in treated effluent (mg/l)	7020.00	2948.40	2035.80	1263.60	919.62	751.14
Amount of Cr removed.(mg/l)	0.00	4071.60	4984.20	5756.40	6100.38	6268.86
% of Cr removed (%)	0.0	58.0	81.0	82.0	86.9	89.3