The Study of Chromium Precipitation from Tannery Effluent
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Abstract:
The study of chromium precipitation from tannery effluent was aimed at comparing the effectiveness of precipitating agents (NaOH, (Ca(OH)₂, MgO) in the removal of chromium from tannery effluents. The dissolved chromium metal was converted into an insoluble form (particle) by chemical reaction between the soluble chromium compound and the precipitating agent. The precipitation process was achieved by adjusting the pH of the tannery effluent to approximately 8.5 by slowly addition of NaOH (precipitating agent). Coagulant was added to enable tiny suspended particle to form larger particle and flocculant was also added to enable the larger particle settle down. After settling the sludge volume was determined. The concentrations of chromium in the tannery effluent before and after precipitation were also determined using Atomic Absorption Spectrometer. The precipitation process was repeated using Ca(OH)₂ and MgO as a precipitating agents. From the result obtained the concentration of chromium before precipitation showed that the tannery effluent is one of the major sources of environmental pollution as the concentration of chromium was very high. However, after chemical precipitation using different precipitating agent, different precipitation having different concentration and sludge volume was observed. The lowest concentration of 0.17 mg/l was observed using MgO as a precipitating agent. The result also showed that the sludge volume produced by MgO was much less than the sludge volume produced by NaOH and Ca(OH)₂. Hence MgO is a good precipitating agent for the removal and recovery of chromium from tannery effluent.

Keywords: Chemical Reaction, Chromium precipitation, Coagulant, Concentration, Flocculant, Pollution, Precipitating agents, Sludge, Spectrometer, Tannery Effluent.

1.0 INTRODUCTION
Chromium solutions are widely used in many industrial processes such as chrome plating, wood preserving, textile dyeing, pigmenting, chromium chemical production, pulp and paper industries, metal finishing and leather tanning. The effluent resulting from these processes contains high amount of chromium metal, which is usually discharged without proper treatment hence causing harm to the environment and human health. Therefore, the removal and reuse of the chromium content of these effluents is necessary for environmental protection and economic reasons (Patterson, 1995). Tannery effluent containing chromium is one of the most obvious problems in leather industry. The tannery wastewater is discharged directly to the main domestic sewage pipeline which adds difficulties to the sewer system and to the wastewater treatment plants. Chromium has been used widely in tanning for the excellent properties that it renders to the leather along with simplicity of operation. However, only 60% -70% of the total chromium salt reacts with the hides. In other word, about 30%-40% of the chromium amount remains in the solid and liquid wastes. As a result of this, the removal and reuse of the chromium content of these wastewaters/effluents is important. In addition, the cost of the chromium metal is also important because it is possible to be recovered from the wastewater (Hafez et al., 2002). Several methods have been used for removing toxic metal ions from aqueous solutions. These include chemical precipitation, ion exchange, reverse osmosis, membrane processes, evaporation, liquid-liquid extraction, and adsorption on coal or activated charcoal, electro-chemical oxidation and reduction, ultra-filtration, bio-precipitation and bio-sorption. Of these, chemical precipitation is the usual way for this purpose. This process transforms dissolved contaminants into an insoluble solid, facilitating the contaminant's subsequent removal from the liquid phase by sedimentation or filtration. The process usually uses pH adjustment, addition of a chemical precipitant, and flocculation (Hafiz et al., 2002). The unit operations typically required in this technology include rapid mixing, precipitation, coagulation/flocculation, sedimentation, decantation and filtration. The effectiveness of a chemical precipitation process is dependent on several factors, including the type and concentration of ionic metals present in solution, the precipitant used, the reaction conditions (especially the pH of the solution), and the presence of other constituents that may inhibit the precipitation reaction (Tsugita, 1999). The most widely used chemical precipitation process is hydroxide precipitation (also referred to as precipitation by pH), in which metal hydroxides are formed by using calcium hydroxide (lime), sodium hydroxide (caustic) or magnesium oxide as the precipitant (Tsugita, 1999).

1.1.AIM AND OBJECTIVES
• Aim
The aim of this research work is to compare the effectiveness of three precipitation agents (calcium hydroxide, sodium hydroxide and magnesium oxide) in the removal of chromium from tannery effluent.

• Objectives
The objective of this research work includes;
a)Analysis of tannery effluent to confirm the present of toxic metal (chromium).
b)Precipitation of chromium from tannery effluent using different precipitating agent.

SCOPE OF WORK: The scope of this research work is to use metal precipitation process for the removal of chromium from tannery effluent using the following processes; rapid mixing,
coagulation and flocculation, sedimentation, decantation and filtration.

1.3 JUSTIFICATION
Tannery effluents are ranked as the highest pollutants among all industrial wastes (Hafiz et al., 2002). They are especially large contributors of chromium pollution because the effluent contains heavy toxic metal which are poisonous to the health of human. They also pose danger to animal, plant and the entire environment. The focus of this research work is to precipitate heavy chromium from a tannery effluent, using chemical precipitation method.

2.0 LITERATURE REVIEW

2.1 TANNERY INDUSTRY
Tanning is the process of making leather, which does not easily decompose, from the skins of animals, which do. It is the process which converts the protein of the raw hide or skin into a stable material which will not putrefy and is suitable for a wide variety of end applications. Traditionally, tanning used tannin, an acidic chemical compound. Colouring may occur during tanning. A tannery is the term for a place where these skins are processed. The principal difference between raw hides and tanned hides is that raw hides dry out to form a hard-inflexible material that when re-wetted (or wetted back) putrefy, while tanned material dries out to a flexible form that does not become putrid when wetted back (Heidemann, 1992). Tanning leather involves a process which permanently alters the protein structure of skin. Making raw hide does not require the use of tanning and is made simply by removing the flesh and then the hair by way of soaking in an aqueous solution (often called liming when using lime and water or bucking when using wood ash (lye) and water), then scraping over a beam with a somewhat dull knife, and then leaving to dry, usually stretched on a frame so that it dries flat. The two aforementioned solutions for removing the hair also act to clean the fiber network of the skin and therefore allow penetration and action of the tanning agent (Heidemann, 1992). Many different tanning methods and materials can be used; the choice is ultimately dependent on the end application of the leather. The most commonly used tanning material is chromium, which leaves the leather, once tanned, a pale blue color (due to the chromium); this product is commonly called "wet blue". The hides once they have finished pickling will typically be between pH 2.8 and 3.2. At this point, the hides would be loaded in a drum and immersed in a float containing the tanning liquor. The hides are allowed to soak (while the drum slowly rotates about its axle) and the tanning liquor slowly penetrates through the full substance of the hide. Regular checks will be made to see the penetration by cutting the cross-section of a hide and observing the degree of penetration. Once an even degree of penetration exists, the pH of the float is slowly raised in a process called basification. This basification process fixes the tanning material to the leather and the more tanning material fixed, the higher the hydrothermal stability and increased shrinkage temperature resistance of the leather. The pH of the leather when chrome tanned would typically finish somewhere between 3.8 and 4.2 (http://en.wikipedia.org/wiki/Tanning).

2.2 CHROMIUM COMPOUND: Chromium is a naturally occurring metallic element. It is found in the soil as well as in volcanic dust and gases. The three major states that occur in the environment are the metallic (zero state), the +3 (III) and the +6 (VI) oxidation states. Chromium III is the most common form which occurs naturally while the 0 and VI forms are usually produced by industrial processes. Chromium metal is a high melting material which has a steel-grey appearance (Baset et al., 1998). Chromium and its compounds are used in many different industries. It is a component of stainless steel and other alloys used in many plating processes. In the chemical industry chromium is used in pigments, metal finishing, leather tanning and wood treatment. It is also used in smaller amounts in textiles, toners for copying machines and in magnetic tapes. Chromium even finds its way into medicine where chromium alloys are used in metallic joint implants in clinical orthopaedics. In general, the largest man-made sources of chromium emissions to the environment are chemical manufacturing, the combustion of fossil fuels, waste incineration and steel making. A significant but smaller source is glass production. Emissions have declined steadily since 1970. Since chromium is also a naturally occurring element in the earth's crust it is also naturally present in the environment at low levels, found in rocks, soils, plants and animals in trace quantities (Randall et al., 1992).

2.2.1 Toxicity of Chromium
The toxicity of chromium is very dependent on the individual chemical compound. The two primary factors that influence the toxicity are the oxidation state of the chromium and the solubility of the compound. Chromium VI which is more commonly used in industry is considerably more toxic that the chromium III state (Ellenhorn et al., 1998). Oral ingestion is almost always intentional and usually causes very severe toxic effects. Ingestion of as little a 1 to 2 grams of potassium dichromate would be lethal. Ingestion causes corrosion of the gastrointestinal tract which is followed by shock. Within several days, multiple organ systems become involved resulting in kidney failure, liver damage and blood disorders including anaemia (Klassner et al., 1996). Chromiums enter the body by oral intake, skin exposure or by inhalation. Any of these routes can result in systemic toxic effects on numerous organ systems. The organs most commonly affected by chromium include the blood forming system, the liver, and the kidneys (Petersburg et al., 1993).

Other health problems that are caused by chromium(VI) are:
- Skin rashes
- Upset stomachs and ulcers
- Respiratory problems
- Weakened immune systems
- Kidney and liver damage
- Alteration of genetic material
- Lung cancer
- Death


2.3.4 Prevention of Exposure
The foremost principle of prevention of exposure is the recognition that the potential for health risk exists. Once the potential hazard is identified and the types of exposure are defined the appropriate steps can be taken to reduce the potential. Since the greatest risk from exposure to chromium occurs for the workers actually using chromium VI compounds through skin contact and by inhalation of fumes, the best means of reducing exposure is to provide protection of exposed skin.
and providing sufficient ventilation and respiratory protective glove and other protective clothing should always be used when there is a chance of contact with chromium solutions or fumes. If workplace ventilation cannot be improved to keep airborne chromium below the recommended levels, then individual respiratory protection should supplement the protective clothing. Because of the potential for development of allergy to chromium, exposure should be reduced to the lowest level that is reasonably possible (Petersburg et al., 1993).

2.4 CHEMICAL PRECIPITATION: Chemical Precipitation is the most common technology used to remove dissolved (ionic) metals from solutions, such as process wastewaters containing toxic metals. The ionic metals are converted to an insoluble form (particle) by the chemical reaction between the soluble metal compounds and the precipitating reagent. The particles formed by this reaction are removed from solution by settling and/or filtration. The unit operations typically required in this technology include neutralization, precipitation, coagulation/ flocculation, solids/ liquid separation and filtration (http://www. waterspecialists.biz/html/whats_new.html). The effectiveness of a chemical precipitation process is dependent on several factors, including the type and concentration of ionic metals present in solution, the precipitant used, the reaction conditions (especially the pH of the solution), and the presence of other constituents that may inhibit the precipitation reaction. The most widely used chemical precipitation process is hydroxide precipitation (also referred to as precipitation by pH), in which metal hydroxides are formed by using calcium hydroxide (lime) or sodium hydroxide (caustic) as the precipitant. Each dissolved metal has a distinct pH value at which the optimum hydroxide precipitation occurs - from 7.5 for chromium to 11.0 for cadmium. Metal hydroxides are amphoteric, which means they are increasingly soluble at both low and high pH values. Therefore, the optimum pH for precipitation of one metal may cause another metal to solubilize, or start to go back into solution. Most process wastewaters contain mixed metals and so precipitating these different metals as hydroxides can be a tricky process (http://www.waterspecialists.biz/html/whats_new.html).

2.4.1 Metal Treatment by Hydroxide Precipitation
As metals enter the treatment process, they are in a stable, dissolved aqueous form and are unable to form solids. The goal of metals treatment by hydroxide precipitation is then to adjust the pH (hydroxide ion concentration) of the water so that the metals will form insoluble precipitates. Once the metals precipitate and form solids, they can then easily be removed, and the water, now with low metal concentrations, can be discharged. Metal precipitation is primarily dependent upon two factors: the concentration of the metal, and the pH of the water. Heavy metals are usually present in wastewaters in dilute quantities (1 - 100 mg/l) and at neutral or acidic pH values (< 7.0). Both of these factors are disadvantageous with regard to metals removal. However, when one adds caustic to water which contains dissolved metals, the metals react with hydroxide ions to form metal hydroxide solids (David et al., 1994).

3.0 METHODOLOGY
Chemical Precipitation method is the most common method used to remove dissolved (ionic) metals from solutions. The ionic metals are converted to an insoluble form (particle) by the chemical reaction between the soluble metal compounds and the precipitating reagent. The particles formed by this reaction are removed from solution by settling and/or filtration. The operations typically required in this technology include rapid mixing, precipitation, coagulation/ flocculation, solids/liquid separation and filtration.

3.1 SOURCE OF TANNERY EFFLUENT: The source of the tannery effluent used in this research work is a tannery wastewater obtained from Kanotan tannery in Kano state, Nigeria.

3.2 LIST OF EQUIPMENT AND APPARATUS

<table>
<thead>
<tr>
<th>S/N</th>
<th>Equipment / Apparatus</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Atomic Absorption Spectrometer</td>
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<tr>
<td>2</td>
<td>Thermometer 0 - 100 °C, glass</td>
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<tr>
<td>3</td>
<td>ph meter 0 - 14 pH, digital</td>
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<tr>
<td>4</td>
<td>500ml Beaker 0 - 500 ml, Pyrex</td>
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</tr>
<tr>
<td>5</td>
<td>500ml Cylinder 0 - 500 ml, Pyrex</td>
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<tr>
<td>6</td>
<td>Magnetic Stirred 500 rpm, electronic</td>
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</tr>
<tr>
<td>7</td>
<td>Filter Whatman 125mm, paper</td>
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</table>

3.3 LIST OF CHEMICALS

<table>
<thead>
<tr>
<th>S/N</th>
<th>Chemicals</th>
<th>Remark</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>Sodium Hydroxide Solution</td>
<td>Analytical reagent, 1M</td>
</tr>
<tr>
<td>2</td>
<td>Calcium Hydroxide Solution</td>
<td>Analytical reagent, 1M</td>
</tr>
<tr>
<td>3</td>
<td>Magnesium oxide Solution</td>
<td>Analytical reagent, 1M</td>
</tr>
<tr>
<td>4</td>
<td>Coagulant (polyamine)</td>
<td>Analytical reagent, 0.5 g/ml</td>
</tr>
<tr>
<td>5</td>
<td>Flocculants (MgS)</td>
<td>Analytical reagent, 0.5 M</td>
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</tbody>
</table>

3.4 PROCEDURE FOR TANNERY EFFLUENT ANALYSIS: The following procedure was carried out to confirm the present of heavy metal (chromium) in tannery effluent.
1. 400ml of effluent was collected in a beaker.
2. The pH value and the temperature of the sample were determined using a pH meter and thermometer respectively.
3. Atomic Absorption Spectrometer was used to determine the concentration of the heavy metal (chromium).

### 3.5 PROCEDURE FOR CHROMIUM PRECIPITATION

1. 400ml of tannery effluent was poured into a 500ml beaker.
2. The solution was heated to approximately 50°C slowly under stirring.
3. The pH was adjusted to approximately 8.5 (optimum pH for Hydroxide precipitation) by slowly adding NaOH (precipitation agent). The pH was monitored using a pH meter.
4. The mixture was stirred using a magnetic stirrer for at least 15 minutes.
5. Five drops of coagulant solution (polyamine) was added to the solution, which was mixed at high speed for two minutes.
6. The stirrer was turned off to allow the coagulation of the precipitated particles. The coagulated particles were allowed to settle by adding approximately five drops of flocculant (magnesium sulphate) to the solution.
7. In order to determine settling rate, the sample was poured into 500 ml scaled cylinders and the sludge volume was read every 30 minute during the settling period.
8. After three hours of settling (when the precipitate has settled down), the precipitate was separated by filtration.
9. The concentration of the metal (chromium) in the filtrate was determined using an atomic absorption spectrometer.
10. Step 1-9 was repeated using solution of lime (calcium hydroxide) and magnesium oxide as the precipitating agents.

### 3.6 DETERMINATION OF CONCENTRATION OF CHROMIUM IN TANNERY EFFLUENT USING ATOMIC ABSORPTION SPECTROMETER

One gram of tannery effluent was weighed into a digestion flask. 5ml of digestion mixture (nitric acid) was introduced into the flask. The sample was digested for three hours at 200-250°C and filtered into 100ml standard volumetric flask with whatman No.1 quantitative circle 125mm filter paper. The filtrate was made up to the mark with distilled water. Since each metal has a characteristics wave length that will be absorbed, chromium cathode lamp was used. The sample was aspirated in to the flame; the chromium metal present in the sample absorbed some of the light hence reducing the intensity of the light. The computer data system converts the change in intensity of light into an absorbance which is directly proportional to the concentration of the chromium metal present in the sample. The concentration of chromium metal present in the sample was determined from the standard calibration curve for chromium metal.

### 4.0 RESULTS AND DISCUSSION

#### 4.1 RESULTS

The results obtain from the experimental investigation were as follows;

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<thead>
<tr>
<th>PARAMETER</th>
<th>AVERAGE VALUES</th>
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<tbody>
<tr>
<td></td>
<td>BEFORE</td>
</tr>
<tr>
<td></td>
<td>PRECIPITATION</td>
</tr>
<tr>
<td>Cr. Conc(mg/l)</td>
<td>6.21</td>
</tr>
<tr>
<td>pH</td>
<td>3.9</td>
</tr>
<tr>
<td>Temp. (°C)</td>
<td>33</td>
</tr>
<tr>
<td>Color</td>
<td>Black green</td>
</tr>
<tr>
<td>Sludge Volume(ml)</td>
<td>-</td>
</tr>
<tr>
<td>Size</td>
<td>-</td>
</tr>
<tr>
<td>Settling Rate</td>
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</table>

![Figure 4.1. Sludge for the Three Precipitation Agents after Three Hours of Settling.](http://ijesc.org/)
4.2 Discussion of Result

The results obtained from this research work are based on the analysis carried out before and after the precipitation of chromium from the tannery effluent. Table 4.1 shows that the average of chromium concentration in the tannery effluent before chemical precipitation was 6.21 mg/l, which is above WHO and FEPA maximum permissible limits of 1.0 mg/l for the discharge of tannery effluent into rivers. This high value of chromium concentration in the effluent is due to the chemical used by tanneries which contain high concentration of this metal. This showed that the effluent from tannery process is one of the most important sources which pollute environment as the concentration of chromium is extremely high. That is why the effluent needs to be treated before disposed. However after chemical precipitation using different precipitating agents, different precipitations having different sizes, settling rate and sludge volume were observed. The concentration of chromium in the tannery effluent using sodium hydroxide (NaOH), magnesium oxide (MgO), and calcium hydroxide (Ca(OH)₂) as precipitating agents was found to be 0.2, 0.17, and 0.21 mg/l respectively. The lowest concentration of 0.17 mg/l was observed using MgO as a precipitating agent. This shows that MgO is the best precipitating agent when compared with NaOH and Ca(OH)₂. This is because when MgO was used as a precipitating agent, it reacts with chromium to form MgCrO₄ which is insoluble and easily precipitates in solution. But when NaOH and Ca(OH)₂ were used as a precipitating agent NaCrO₄ and CaCrO₄ are formed respectively which are less insoluble compare to MgCrO₄. Settling rate is one of the key factors in precipitation process since it governs the precipitation efficiency and performance. From the settling behaviour (obtained by reading the sludge volume during the settling period) it was observed that when MgO was used as a precipitating agent, the settling rate was faster, compared to when Ca(OH)₂ and NaOH were used as a precipitating agent. The precipitation forming from NaOH has a very small size and settling rate of precipitation was very slow. Using Ca(OH)₂ as precipitant can improve velocity of settling, but the improvement was little and the precipitation size was also small. However, grainy and large precipitation with higher settling rate was obtained by MgO. Figure 4.1 shows the sludge for the three precipitation agents after three hours of settling period. The sludge volume produced when magnesium oxide (MgO), calcium hydroxide (Ca(OH)₂) and sodium hydroxide (NaOH) were used as precipitating agents was found to be 51ml, 155ml and 260ml respectively. This shows that sludge volume produced by MgO is much less than sludge volume produced by Ca(OH)₂ and NaOH. Hence a good precipitation with fast settling rate and lower volume of sludge can be achieved using MgO because of its low solubility. The chromium concentration in the filtrate solution using the three precipitating agent was below WHO and FEPA limit of 1.0mg/l. Thus any of the three precipitating agent can be used in the removal and recovery of chromium from tannery effluent before disposal. However, a grainy, dense, easily settable and filtrate precipitation can be formed only when MgO is used as the precipitant.

5.2 RECOMMENDATIONS

1. Other precipitating agent which can also be used to precipitate chromium from tannery effluent should be used and the result compared.
2. Domestic water source i.e. springs, well or surface water should be protected against contamination by the tannery effluent.
3. The mean concentration of chromium in tannery effluent should be monitored strictly by relevant authorities in order to prevent environmental pollution and reduce health hazards caused by this pollution.
4. FEPA/ministry of environment should intensify their industrial pollution abatement drive, especially among the small scale industrialists whom are gradually becoming a great source of environmental pollution.

5.0 CONCLUSIONS AND RECOMMENDATION

5.1 CONCLUSIONS

The results of this study showed that the effluent from tannery process is one of the most important sources of environment pollutants as the concentration of chromium in the effluent was extremely high. Sludge volume by MgO is much less than sludge volume produced by Ca(OH)₂ and NaOH. The average ratio of sludge volume produced by the three precipitating agents after three hours of settling is: \( V_{MgO} : V_{Ca(OH)₂} : V_{NaOH} = 1 : 2.3 : 5.1 \). Good sludge with high settling rate and lower volume was obtained when using MgO as the precipitating agent. Hence the MgO is a good precipitating agent for removal and recovery of chromium from tannery effluent.


