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# Treatment of Tannery Effluents by the Process of Coagulation

G. Shegani

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***Abstract*—**Coagulation is a process that sanitizes leather effluents. It aims to reduce pollutants such as Chemical Oxygen Demand (COD), chloride, sulfate, chromium, suspended solids, and other dissolved solids. The current study aimed to evaluate coagulation efficiency of tannery wastewater by analyzing the change in organic matter, odor, color, ammonium ions, nutrients, chloride, $H_2S$, sulfate, suspended solids, total dissolved solids, fecal pollution, and chromium hexavalent before and after treatment. Effluent samples were treated with coagulants $Ca(OH)_2$ and $FeSO_4 \cdot 7H_2O$. The best advantages of this treatment included the removal of: COD (81.60%); ammonia ions (98.34%); nitrate ions (92%); chromium hexavalent (75.00%); phosphate (70.00%); chloride (69.20%); and $H_2S$ (50%). Results also indicated a high level of efficiency in the reduction of fecal pollution indicators. Unfortunately, only a modest reduction of sulfate (19.00%) and TSS (13.00%) and an increase in TDS (15.60%) was observed.

***Keywords*—**Coagulation, Effluent, Tannery, Treatment.

## I. Introduction

An important environmental impact of the leather industry is its high pollution load of wastewater. Tannery effluents affect the receiving water quality in multiple ways:

1. The discharge of biodegradable organic compounds causes a strong reduction in the amount of dissolved oxygen in surface waters.
2. Macro-nutrients such as phosphorus and nitrogen may cause eutrophication of the receiving water bodies.
3. Tannery effluents may contain compounds that are directly toxic to aquatic life such as chromium and un-ionized ammonia [16].

Thus, treatment of tannery wastewater is always required. It is an obligatory process that sanitizes leather effluents in order to avoid degradation of the receiving terrestrial and aquatic systems in the vicinity of the discharge points [5]. More specifically, the goal is to rid the wastewater of pollutants such as organic matter, chloride, sulfate, sulfide, nutrients, chromium, suspended solids, and other dissolved solids. Objectives of coagulation typically include lower water consumption, improved uptake of chemicals, better quality/re-usability of solid waste, and reduced content of specific pollutants such as heavy metals and electrolytes [1].

Various physic-chemical techniques have been studied for their applicability to the treatment of tannery wastewater. Among these are coagulation, flocculation, ozonation, reverse osmosis, ion exchange, and adsorption. Coagulation and flocculation, which are understood as being part of the second stage of the coagulation process, are two distinct processes usually carried out as a combination of physical and chemical procedures during primary treatment of tannery effluents.

The most frequently used coagulants in tannery effluent treatment are:

- Industrial Aluminum Sulfate: $Al_2(SO_4)_3 \cdot 18H_2O$
- Industrial Iron Sulfate: $FeSO_4 . 7H_2O$
- Industrial Iron Chloride: $FeCl_3 . 6H_2O$
- Industrial Calcium Hydroxide: $Ca(OH)_2$

Coagulation is not a perfect process. Thus, further treatments known as biological (secondary) and advanced (tertiary) treatment are required in the leather industry in order to meet proposed tannery effluent standards [2].

The current study evaluated coagulation efficiency of tannery wastewater. The reduction of organic matter, odor, color, ammonium ions, nutrients, chloride, $H_2S$, sulfate, suspended solids, total dissolved solids, chromium hexavalent were all taken into account. Fecal pollution indicators (*Escherichia coli*, *Streptococcus faecalis*) were also used to analyze bacteriological pollutants.

## II. Related Research

A number of studies have investigated coagulation of tannery effluents in different ways with various types of coagulants [2]-[4]. Coagulants $FeCl_3$, $Al_2(SO_4)_3 \cdot 18H_2O$, $Ca(OH)_2$, $Al_2(SO_4)_3 \cdot 18H_2O$ and $Ca(OH)_2$ are known to produce better results than $FeCl_3$ in terms of COD, color, and Cr removal [2]. Conversely, $Al_2(SO_4)_3 \cdot 18 H_2O$ and $FeCl_3$ produced the least amount of sludge in comparison to $Ca(OH)_2$. Tannery effluents have also been treated with commercial grade lime [3]. Low values of COD and the removal of chromium, TSS, TDS were observed in this investigation. Results from a similar study suggest that untreated tannery effluents can also be treated by a combined process of settling, filtering, and coagulation with $FeCl_3$ [4].

## III. Materials and Methods

A 1000mL sample of effluent was collected in a polyethylene container that was previously washed with diluted $HNO_3$. The sample originated from the main drainage reservoir of tannery facility before it was discharged directly into river water (there was no sedimentation tank). Within 15 minutes, the effluent sample was treated with coagulants $Ca(OH)_2$ and $FeSO4 \cdot 7H_2O$. 1000mg of each coagulant was mixed well with 1000mL of the effluent sample for 15 minutes. The mixture then sat undisturbed for 24 hours in the dark at room temperature.

Gentiana Shegani is with the Directory of Public Health, Berat, Albania; (e-mail: gentashegani@hotmail.com).

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The basic equation occurring during coagulation for ferrous sulfate is given by the equation:

$$FeSO_4 + 2\,HCO_3^- \rightarrow Fe(OH)_2 + SO_4^{-2} + 2CO_2$$

During coagulation, hydrolysis of $FeSO_4$ results in the formation of hydroxides and some positively charged mononuclear and polynuclear species. These positively charged compounds combine with negatively charged colloidal particles present in the wastewater via charge neutralization. Once they settle under gravitational forces, these hydroxides and complexed hydroxides sweep away the remaining uncharged/charged colloidal particles of the wastewater with and precipitate out [7]. $Ca(OH)_2$ operates as a coagulant aid to add density to slow-settling flocks [10].

After settling and interacting with the coagulants, the effluent sample remained in a 1000 mL graduated transparent cylinder for 30 minutes. The settled sludge volume was then measured in mL/L and the supernatant liquids were separated from the deposited sludge and passed through medium filter paper (120 mm diameter). After coagulation, sedimentation, and filtration, collected effluents were analyzed for various physic-chemical and bacteriological parameters.

## IV. Results

A total of 17 different effluent samples were collected over a period of six months. Physical, chemical, and microbiological characteristics of the tannery effluents were analyzed before and after coagulant treatment. The obtained results and a summary of basic statistics of tannery wastewaters before and after treatment with coagulants and filtration processes are presented in Table I.

Mean values of the effluent ranged from 20°C-33°C before treatment in natural conditions and from 19.5°C - 26°C after treatment in laboratory conditions. The results indicate that the color of both treated and untreated leather effluents did not significantly differ from one another. This may be due to the high content of dissolved solids. Experimental results indicated a substantial change in the odor of the wastewater. The odor was very strong in untreated effluents and significantly less potent after treatment. However, effluents regained their characteristic odor once the effluent samples were treated with heat (i.e. boiling).

It is possible for alkalinity and high pH values to be present naturally in tannery wastewater [10]. With the addition of $Ca(OH)_2$ as a coagulant (1000mg/L) in effluents, it would achieve the highest values. However, the results did not indicate these findings (Fig. 1). pH values ranged from 9.36 before treatment to 9.305 after treatment. These values are closely related to the total values of alkalinity, which ranged from 206.12 mg/L $CaCO_3$ before treatment to 197 mg/L $CaCO_3$ after coagulation. This negligible difference in pH and total alkalinity could possibly attribute to the presence of $FeSO_4 \cdot 7H_2O$ as a co-coagulant in the treatment.

TABLE I
PHYSICAL, CHEMICAL, AND MICROBIOLOGICAL CHARACTERISTICS OF TANNERY EFFLUENTS

| Parameters | Minimum | Maximum | Mean | Median | Standard Deviation | Coefficient of Variation | Threshold X + 2S |
|---|---|---|---|---|---|---|---|
| pH | 8.9 – 8.7 | 10.8 – 10.5 | 9.36 – 9.305 | 9.2 – 9.3 | 0.48 – 0.42 | 0.05 – 0.045 | 10.31 – 10.14 |
| Total Alkalinity (mg/L $CaCO_3$) | 123 – 100 | 380 – 350 | 206.11-197 | 178-184 | 67.39 – 74.93 | 0.32 – 0.38 | 340.90 – 346.86 |
| Ammonium Ions | | | | | | | |
| $NH_4^+$ (mg/L) | 1.5-0.1 | 30-8 | 9.08-1.65 | 8-1 | 7.1-1.93 | 0.78-1.16 | 23.28-5.51 |
| Nitrate ions | 5-1 | 70-15 | 37.06-6.06 | 35-5 | 22.91-5.54 | 0.618-0.91 | 82.87- 17.15 |
| $NO_3^-$ (mg/L) | | | | | | | |
| Phosphates (mg/L) | 0.1-0.1 | 20-8 | 8.36-2.51 | 5-2 | 6.79-2.67 | 0.81-1.06 | 21.39-7.85 |
| Chloride (mg/L) | 177.25-128.5 | 30205-2836 | 3814.63-1176.7 | 2516-1063.5 | 6294.61-799 | 1.81-0.68 | 17663.85-2774.8 |
| COD (mg/L $O_2$) | 88-47.2 | 2560-1260 | 545.8-232.2 | 304-142 | 646.5-285.2 | 1.18-1.23 | 1838.8-802.6 |
| Sulfate (mg/L) | 53.49-3.7 | 2492.04-2586.4 | 818.8-665.8 | 377.3-318.56 | 744.9-715 | 0.9-1.07 | 2308.67-2095.9 |
| TSS (mg/L) | 41-33 | 9955-14174 | 2196.35-1923.6 | 334-310 | 3204.04-3970.31 | 1.45-2.06 | 8604.4-9864.2 |
| TDS (mg/L) | 1670-2272 | 31295-32269 | 5966.1-7068.2 | 3916-4766 | 6780.9-7027.1 | 1.14-0.99 | 19528-21122 |
| Chromium (VI) (mg/L) | 0.1-0.01 | 0.5-0.15 | 0.195-0.056 | 0.2-0.05 | 0.094-0.033 | 0.48-0.58 | 0.3-0.12 |
| $H_2S$ gas (mg/L) | 115.6-47.6 | 595-255 | 255.7-128.26 | 170-119 | 145.7-61.56 | 0.57-0.48 | 547.12-251.4 |
| Iron ions (mg/L) | | | | | | | |
| $Fe^{2+}/Fe^{3+}$ | 0.01-0 | 1-0 | 0.126-0 | 0.02-0 | 0.247-0 | 1.96-0 | 0.62-0 |
| Fecal Coliform | | | | | | | |
| *Escherichia* coli (MPN)[a] | 1609-14 | >1609-542 | >1609-220.4 | 1609-221 | 0-145.49 | 0-0.66 | >1609-511.39 |
| *St. faecalis* (MPN) | 918-17 | 1609-348 | 999.3-138.4 | 918-140 | 229.5-91.69 | 0.23-0.66 | 1458.25-321.79 |

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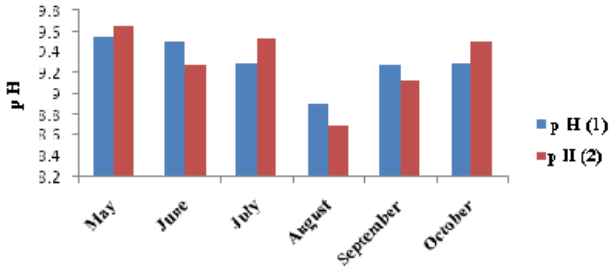



Fig. 1 Monthly variation in mean pH values before (1) and after (2) treatment with coagulants

It is well known that pH is an important factor of the coagulation process [2]. The use of coagulants at the optimal pH level has been shown to maximize the removal of pollutants [2]. The maximum percentage of COD removal was 81.60%, for ammonia ions 98.34%, for nitrate ions 92% and for chromium hexavalent removal 75% were obtained at the optimal pH value of 8.7. Furthermore the quantities of microorganisms (*Escherichia coli* and *Streptococcus faecalis*) as indicators for the fecal pollution of effluents were reduced by 94.15% and 92.4%, respectively. Conversely, the maximum reduction of microbiological load pollution obtained was 97.14% for *Escherichia coli* and 97.60% for *Streptococcus faecalis* at the pH value of 9.5. Fig. 3 illustrates the change in phosphate concentration before and after treatment (8.36 mg/L before - 2.51 mg/L after). The reduction of phosphates by 70% was attributed to the use of the coagulants. $FeSO_4 \cdot 7H_2O$ in particular has proven to be effective in reducing phosphorus, fats, oils, and greases, to minimize hydrogen sulfide release [17].

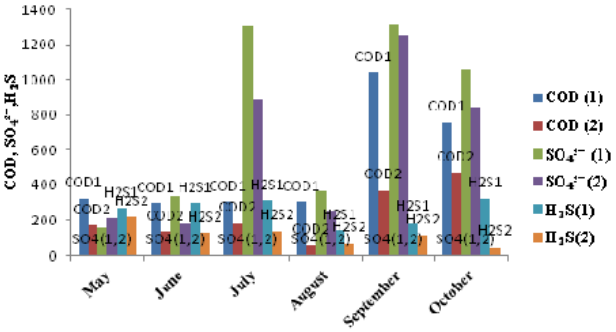



Fig. 2 Monthly variation of average COD, $H_2S$, and $SO_4^{2-}$ before (1) and after (2) treatment

COD mean values varied between 545.8-232.2 mg/L $O_2$ whereas $H_2S$ ranged from 255.74-128.26 mg/L (Fig. 2). $H_2S$ is known to be present only at pH levels below 10 [1]. As a result of coagulation, the amount of $H_2S$ reduced by 50%. Optimum $H_2S$ removal (85.4%) was achieved at a pH value of 9.5. Mean values of $SO_4^{2-}$ varied from 818.82-665.8 mg/L after coagulation.

High concentrations of $SO_4^{2-}$ in tannery effluents result from many auxiliary chemicals containing sodium sulfate as a byproduct of the manufacturer or chrome tanning powders [1]. In this study, the amount of $SO_4^{2-}$ was reduced by 19%. This may be due to the large amount of ferrous sulfate (1000mg) in 1 liter effluents. $FeSO_4 \cdot 7H_2O$ is a coagulant already known to give optimal results in lower doses during the chemical treatment of industrial wastewater [6].

Final results indicate that there was a decrease of ammonium ions by 82%, pH by 0.6%, and total alkalinity by 4.5%. Nitrate ions ranged from 37.05 (mg/L) - 6.05 (mg/L); an overall decrease of 83.6% as shown in Fig. 3. COD was also reduced by 57.5% and chromium (VI) by 71.3%.

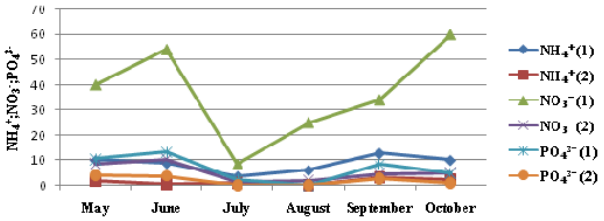



Fig. 3 Monthly variation of mean $NH_4^+$, $NO_3^-$, $PO_4^{3-}$ values in untreated (1) and treated (2) leather effluents

Results showed high efficiency in the decrease of fecal bacteria during coagulation. MPN mean values ranged higher than 1609/100 ml - 220/100 ml for *E. coli* and 999/100ml-138/100 ml for *St. faecalis*. MPN for *E. coli* was reduced by 86.30% and 86.15% for *St. faecalis*. Coagulants were effective in removing fecal pollution because they produced a large volume of flocks – entities known for their ability to entrap bacteria as they settle [11]. Large quantities of chloride are usually introduced into tannery effluents as sodium chloride usually in the form of common salts used for animal hide and skin preservation or the Pickling Process. Being highly soluble and stable, chlorides are unaffected by effluent treatments. Thus, they end up inflicting a burden upon the environment [9].

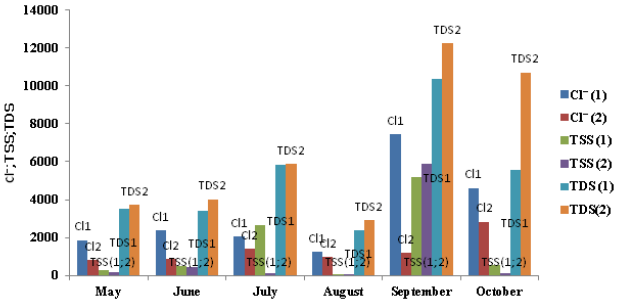



Fig. 4 Monthly variation of average Chloride, TSS, and TDS values before (1) and after (2) coagulation

The concentration of chloride ranged from 3814.63 mg/L before treatment to 1176.67 mg/L after treatment – a reduction of 69.20% (Fig. 4). The mean values of total suspended solids (TSS) ranged from 2196.35 mg/L before to 1923.6 mg/L after treatment. The average values of total dissolved solids (TDS) ranged from 5966.11mg/L before to 7068.23mg/L after coagulation. Treatment results illustrated that TSS decreased

by 13% and TDS increased by 15.6%. TSS and TDS removal efficiency during coagulation, however, was very low. This may have occurred as a result of excessive doses of coagulants - especially ferrous sulfate, which had a concentration of 1000mg/L.

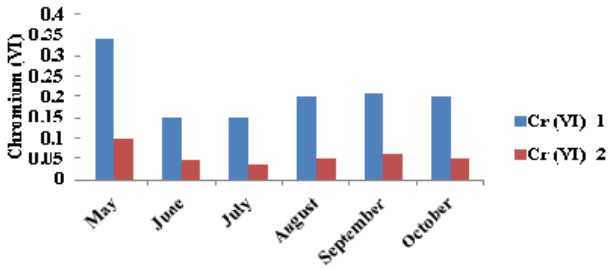



Fig. 5 Monthly variation of average Chromium Hexavalent values in untreated (1) and untreated (2) effluents

Metal compounds are not biodegradable. Thus, they can be regarded as long-term environmental hazards. Tannery effluents contain the metal compound Chromium Hexavalent. Dichromates are toxic to aquatic life since they swiftly penetrate cell walls of aquatic animals like fish. Chromium (VI) is mainly absorbed through the gills of fish and its effect has been found to be cumulative [9]. The mean values of Chromium Hexavalent ranged from 0.2mg/L before treatment to 0.055mg/L after treatment by coagulants – an overall reduction of 71.30%. The optimum Chromium (VI) removal (75%) occurred at pH values of 8.7 and 9.5 in August and October, respectively (Fig. 5).

A large amount of sludge is generated when physic-chemical treatment is applied to wastewater during coagulation-flocculation. Thus, when a coagulant is used, it is important to consider how much sludge will be produced [2]. Indeed, Ca $(OH)_2$ is very effective in the removal of COD, chromium, odor, ammonium ions, and nutrients; however, it produces additional sludge [2]. The Sludge Volume Index (SVI) is the volume in milliliters occupied by 1 gram of a suspension after settling in a 1000 ml graduated cylinder or Imhoff cone for 30 minutes [1]-[12]. SVI is typically used to monitor settling characteristics of activated sludge and other biological suspensions [12]. SVI is calculated with the following basic formula:

$$SVI = \frac{Settled\ Sludge\ Volume\ {}^{mL}/_{L} \times 1000}{Suspended\ Solids\ {}^{mg}/_{L}}$$

In this study, the mean value of SVI was 85.6 mL/mg (Fig. 6). Well settled and mineralized sludge has an SVI < 100 (mL/mg) [1].

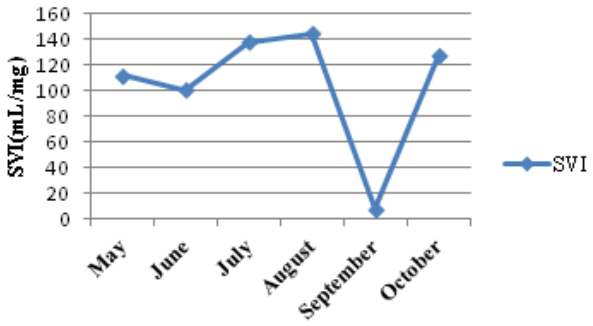



Fig. 6 Monthly variation of SVI

## V. Conclusion

This study demonstrated how efficient physic-chemical treatment can be when coagulating raw tannery effluents with $Ca(OH)_2$ and $FeSO_4 \cdot 7H_2O$. Physic-chemical and bacteriological parameters have exceeded many times the standard prescribed limits in the past [13]-[15]. The new findings presented in these current results illustrate how advantageous $Ca(OH)_2$ and can be when coagulating raw tannery effluents. Disadvantages of this study revolve around the relatively low reduction of sulfate and TSS and the increase in TDS. Due to the high quantities of coagulants used in this study, it is possible that it is more effective for the lowest volume of settled sludge and required coagulant doses to be lower than 1,000 mg/L. In order for tannery wastewater to be safely discharged into the local aquatic environment, the author recommends that some of the pollutants within it be treated further before being released.

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