

Extraction of Chromium Six from Chrome Shavings

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Abstract— The chrome shavings which constitute 2.5-5% chromium are mainly disposed at the outside premises of the tannery and left to dry, posing a hazardous environment. When the chrome shavings are dried they would be taken by brick - makers and burnt out, a process which will transform chromium III to chromium VI. Chromium VI is 500 times toxic than chromium III and most harmful pollutants in tannery waste. Chromium VI also affects soil quality, more dangerous and carcinogenic. Therefore recovery of chromium VI is very essential. In this study chrome shavings was incinerated at 1000°C to transform chromium III to chromium VI. Leaching of chromium VI in form of dichromate was done in a series of 6 batteries and statistically investigated at different levels of solid/liquid ratios, temperatures, degree of mixing and time. Further evaporation was done in a triple-effect evaporator to raise up the concentration from 40% to 90%. From the statistical analysis it is determined that only the degree of mixing at 200rpm is significant, and other factors are fixed at their low levels, temperature of 37°C, time of 1 hour and solid/liquid ratio of 1:10.

Index Terms— chromium VI, leaching, chrome tanning, solid waste, triple effect evaporator

I. INTRODUCTION

The major process of the tanning industry is chrome tanning which produces leathers characterized by top handling quality, high hydro-thermal stability and excellent properties [1]. The majority of the shoe uppers are tanned with chromium compound [2]. Leather manufacture is steadily increasing the use of chromium compounds in the manufactures of various types of leathers such as garment, clothing, gloving, bags, textile and furniture [2]. Tanneries produce a great variety of waste, in particular, the solid waste coming from the leather tanning with trivalent chromium

salts as trims and shavings. These need special treatment due to environmental regulations and the controlling laws requirements for those wastes [3]. Most of the tanneries around the world discharge 25-40% of total basic chromium sulfate used in the tanning process. Basic chromium sulfate containing trivalent chromium has been recognized as a less toxic compared with the hexavalent form which is more toxic and carcinogenic. Many noxious residues are routinely treated for recovery of heavy metals, with techniques that include conventional neutralization, precipitation, reduction, separation and solvent extraction [4].

Shaving process is to adjust the thickness to make the wet blue pelts ready for retannage and the following processes. Shaving is carried out by a shaving machine taking off about 20% of the wet- blue pelt weight from the flesh side. One tone of raw wet hides produces 200 kg of leather but produces over 600 kg of solid waste or byproduct [5,6]. It has been stated that about 600,000 tones of solid waste are generated each year worldwide by the leather industry, this means that approximately 40-50% of hide substance are lost due to shavings and trimmings [7]. A chrome shaving constitutes 75% of the solid waste containing chromium in the tanning process, beside the 30-35m³ waste water disposed to the environment during the processing of every one ton of raw hides in world leather industry, the data obtained from FAO reveals that approximately 8.5 million tons of solid waste is generated during the production of 11 million tons of rawhide processed in the world which is in agreement with the fact stated that 60% of solid waste is generated [6, 8]. There are twelve working tanneries in Sudan processing wet blue of different capacities. The total amount of wet blue pelts processed are about 850 thousand tons per year and about 4-6 thousand tons of basic chromium sulfate in the chrome tannage operations. The objectives of this study, to transforming chromium III to chromium VI as a raw material for reduction to basic chromium sulfate, to specify the conditions for optimum leaching of chromium VI and to adjust the basicity of basic

chromium sulfate to 33% basicity rendering it suitable for chrome tannage.

II. MATERIALS AND METHODS

Analysis of chrome shavings

Chrome shavings were collected from the incubator of the faculty of engineering, Sudan University of Science and Technology, dried at room temperature for seven days and analyzed using official methods of analysis [9] for chromic oxide, moisture and ash contents. The chrome shaving was burnt in a furnace for two hours at 1000°C to transform chromium III to chromium VI (Thermolyne Benchtop Muffle Furnace).

Analysis of chrome shaving ash, Chromium content and Total soluble

10.0 g of chrome shavings ash were extracted in soxhlet apparatus using 250 mL distilled water until the recycled solution became clear. The residue was taken and weighed, and the solution is analyzed using spectrophotometer (Cary 100 Perkin-Elmer UV–visible spectrophotometer).

Preparation of standard solutions for Spectrometry

Standard solution that contains 1000 ppm of chromium was prepared; 10 ppm was taken and diluted to 100 mL. Five working standard solutions of 5, 10, 15, 20, 25 ppm were prepared in 50 mL volumetric flask.

Leaching

Leaching of dichromate was carried out using distilled water in a series of single contact batch experiments to determine the effect of the various factors on leachability of dichromate from shavings ash. Factors which normally influence the rate of extraction of a solute from a solid are:

- Time of leaching
- Leaching temperature
- Degree of mixing
- Solvent-solid ratio

Time of leaching

10.0 g of chrome shavings ash were taken in a beaker, 100 mL of distilled water were added at 38°C and left for 1 hour with mixing, the beaker contents was filtered, the extract was analyzed for concentration of dichromate and then subjected to more leaching using same conditions described above, this process was repeated 10 times until the recycled solution was clear.

The rate of transfer from the particles to the bulk of the liquid is correlated and found to be:

$$C = C_s (1 - e^{-t}) \text{-----(1) [10] where :}$$

C: concentration of the solute at any time t.

C_s : chromium VI content in chrome shavings ash.

t: time

Evaporation

2000.0 kg/h of 40% sodium dichromate solution is fed to a triple-effect evaporator to raise the concentration of the dichromate to 90%. The outlet solution obtained is 888.9kg/h

and the water evaporated is 1111.1 kg/h. saturated steam at 1.2 atm and 110 °C is used for heating as shown in Fig 1.

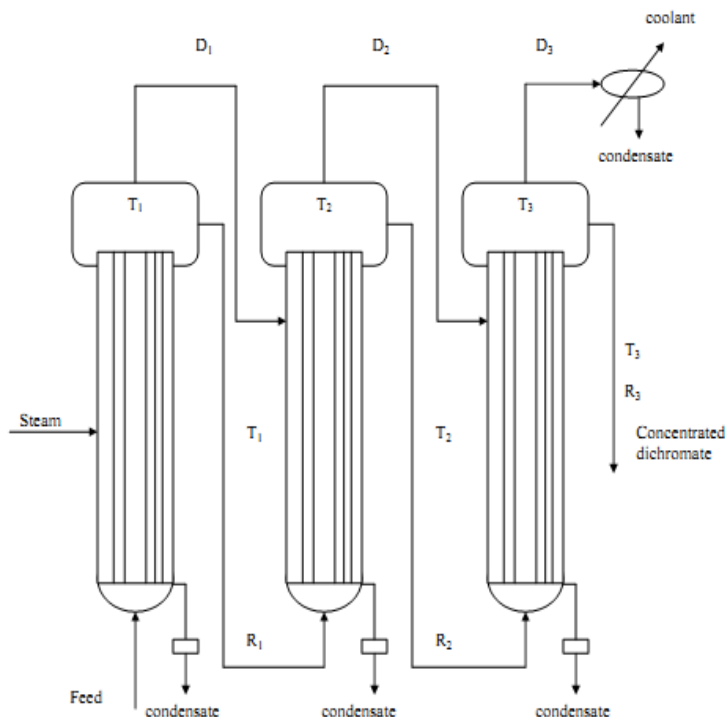


Figure 1: Flow sheet of triple- effect evaporator

III. RESULTS AND DISCUSSION

The chemical analysis of chrome shavings collected from the incubator shows that chromic oxide content was found to be 2.7% which is quite significant as shown in Table 1.

Table 1
Analysis of chrome shavings

Characteristic	Contents
Average moisture (%)	13.9
Ash content(% dry weight)	8.5
Chromic oxide(% dry weight)	2.75

The incineration of chrome shavings at 1000°C oxidized all chromium III to chromium VI. The energy produced from the incineration of chromium III can be utilize for steam generation needed for retanning, fatliquoring and dyeing processes.

The analysis of chrome shavings ash are 1.6 g/L of dichromate

Item	Content
Dichromate	1.6 g/l
Total soluble	50.85%

and the total solubility is 50.85 % as shown in **Table 2** which are significant.

Table 2
Analysis of chrome shaving ash

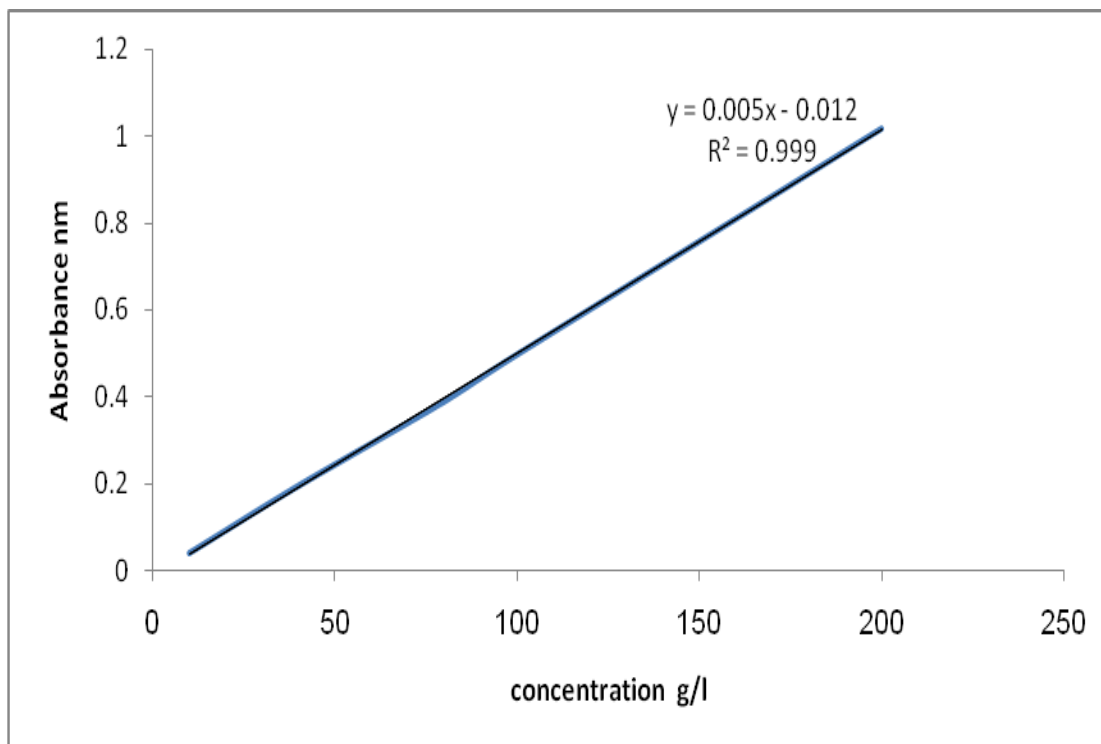


Figure 2: Calibration and correlation of chromium VI.

The blank solution and the standard solutions of the chromium are analyzed with atomic absorption spectrophotometer and a linear calibration curve is drawn, **Fig 2**.

Two level factorial experiments were carried out to investigate the effects of the above factors and their significance as shown in **Table 3**.

The actual levels are:

A: (1, a) time, 1 hour and 3 hours.

B: (1, b) temp 38⁰C and 70⁰C.

C: (1, c) without mixing, with mixing at 200 rpm

D: (1 , d) solid/solvent ratio, 1:10, 1:30

The number 1 indicates that the chosen factor is at its low value, and a,b,c,d indicate that the factors are at their high values. Each experiment was replicated.

Table 3
Factorial experiments for the factors influence leaching

Treatment combination	Time hour	Temp °C	Solvent/solid ratio	Mixing rpm	Concentration mg/L
1	1	37	1:10	without	37.2
A	3	37	1:10	without	38.2
B	1	70	1:10	without	37
C	1	37	1:30	without	45.6
D	1	37	1:10	With mixing	36.2
Ab	3	70	1:10	without	37.4
Ac	3	37	1:30	without	49.8
Ad	3	37	1:10	With mixing	39.8
Bc	1	70	1:30	without	52.8
Bd	1	70	1:10	With mixing	35.4
Cd	1	37	1:30	With mixing	55.2
Abc	3	70	1:30	without	55.2
Abd	3	70	1:10	With mixing	45.4
Bcd	1	70	1:30	With mixing	56
Acd	3	37	1:30	With mixing	47.4
Abcd	3	70	1:30	With mixing	55.6

The leaching of dichromate was statically investigated at different factors. It was found that only the degree of mixing of 200 rpm is significant. This is due to rapid contact of the solvent with the solute inside the potteries. Other factors of time, temperature and solid/solvent ratio are non significant and are used at their low level as shown in **Table 4**.

2000.0 kg/h of 40% concentration of sodium dichromate solution is prepared. This is fed into a single- effect evaporator to raise the concentration of the dichromate from 40% to 90%. The steam quality is saturated steam at atmospheric pressure with latent heat of condensation of 1998 kJ/kg. The steam

consumption is 114.4 kg/h while the steam economy is 0.9 which is less than 1.0. Hence a double- effect evaporator is tried using the same feed and the same product concentration; this gives a steam economy of 1.4. However for maximum steam economy a triple- effect evaporator shown in Fig. 1 is used for the same feed conditions giving a steam economy of 1.7, this is found to be the better steam economy and therefore it is used in this research. The concentrated solution is spray dried giving sodium dichromate as a powder which can further be reduced to basic chromium sulfate with sugar or molasses.

IV. CONCLUSIONS

It is concluded that chrome shavings instead of being taken by brick makers and producing chromium VI, it will be incinerated and reduced to basic chromium sulfate which can be recycled

for chrome tannage. The heat liberated in the incinerator can be used to generate steam for fatliquoring and dying process. The environment is thus protected from any possibility of disposing chromium VI which is toxic and carcinogenic.

Table 4
Concentrations of chromium VI at different factors and their significance

The factor	Number of experiments	mean	Std. deviation	Std. error mean	Significant
Solvent/liquid ratio					
Concentration:					
Low	8	42.56	8.44	2.98	NS
high	8	44.25	9.23	3.26	
Temperature					
Concentration:					
Low	8	42.88	8.40	2.97	NS
high	8	43.94	9.32	3.29	
Time					
Concentration:					
Low	8	41.69	8.48	2.99	NS
high	8	45.12	8.91	3.15	
Degree of mixing					
Concentration:					
Low	8	35.62	1.97	0.699	Sig
high	8	51.19	3.98	1.40	

NS = not significant

Sig = significant

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