



e-ISSN: 2319-8753 | p-ISSN: 2347-6710

IJRSET

International Journal of Innovative Research in
SCIENCE | ENGINEERING | TECHNOLOGY

INTERNATIONAL JOURNAL OF INNOVATIVE RESEARCH

IN SCIENCE | ENGINEERING | TECHNOLOGY

Volume 12, Issue 9, September 2023

ISSN INTERNATIONAL
STANDARD
SERIAL
NUMBER
INDIA

Impact Factor: 8.423

 9940 572 462

 6381 907 438

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 www.ijrset.com

Experimental Removal of Chromium from Tannery Solid Waste

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ABSTRACT: The determination of Chromium containing leather wastes to simplify the recovery of its considerable protein fractions. Organic salts and acids such as potassium tartrate and acetic acid were tested for their efficiency to separate the chromium from leather waste. My investigation is based on the research of the total reversibility of the tanning process, in order to decontaminate the waste without its previous degradation or digestion. The effect of several influential parameters on the treatment process was also studied. Therefore, the action of chemical agents used in decontamination process seems very interesting. The optimal yield of chromium extraction about 95% is obtained. The aim of the present study is to define a preliminary processing of solid leather waste with two main impacts, Removing chromium in the tanning process with simple, ecological and economic treatment process and potential valorization of the organic matters of waste decontamination

I. INTRODUCTION

Leather industry provides the necessities, such as leather shoes and garments. While using the byproducts of the meat industry. In turn, it generates by products and wastes. It is known that only 20% of wet salted hides/skins are converted into commercial leather, while 25 % becomes chromium containing leather wastes (CCLW), and the remainder becomes non-tanned waste or is lost in wastewater as fat, soluble protein and suspended solid pollutants. Environmental pollution is a difficult problem for world leather industry. In past decades, a lot of efforts has been made to study the soil collagenous wastes, including isolation of protein products from CCLW. Unfortunately, most of these processes reported bring about new residues during treatment. In recent years, China has been the largest leather manufacturing country, typically from pigskin processing.

CHROMIUM:

Naturally occurring chromium is usually present as trivalent Cr(III), Hexavalent Cr(VI) in the environment is almost totally derived from human activities [WHO 1990]. According to the Toxics Release inventory, in 1997, the estimated release of chromium was 706,204 pounds to the air from 3,391 large processing facilities which accounted for about 2.2% of total environmental releases. Cr (III) and Cr (VI) are released to the environment primarily from stationary point sources (facilities that are identified individually by name and location) resulting from human activities. The estimates of atmospheric chromium emissions in 1976 and 1980 in the Los Angeles, CA and Houston, TX areas indicated that emission from stationary fuel combusting are about 46-47% of the total, and emissions from the metal industry range from 26 to 45 % to the total [ATSDR 2000].

Chromium picolinate is a popular supplement often marketed to those wanting to build muscle or lose weight. Some bodybuilders and athletes take it to enhance performance and increases energy. Early studies suggested that supplemental chromium may contribute to weight loss and help increase muscle mass. These studies were not conclusive, but more recent studies have shown improved muscle growth or a decrease in fat mass. In addition, the amount of weight loss was not considered sufficient to make supplements worthwhile. Some of those taking the supplement also experienced side effects, including watery stool, vertigo, headaches and hives.

SOURCE OF CHROMIUM:

Coal and Oil combusting contribute an estimated 1,723 metric tons of chromium per year in atmospheric emissions; however, only 0.2% of this chromium is Cr (VI). In contrast, chrome plating sources are estimated to contribute 700 metric tons of chromium per year to atmospheric pollution, 100% of which is believed to be Cr (VI)[ATSDR 2000].

Cr(III) in the air does not undergo any reaction. Cr (VI) in the air eventually reacts with dust particles or other pollutants to form Cr (III). However, the exact nature of such atmospheric reactions has not been studied extensively [EPA 1998].

According to the Toxics Release Inventory, in 1997, the estimated releases of chromium was 111,384 pounds to water from 3,391 large processing facilities which accounted for about 0.3% of total environmental releases [ATSDR 2000].

POLLUTANTS:

In the past decades the increased use of Chromium (Cr) in several anthropogenic activities and consequent contamination of soil and water has become an increasing concern. Cr exists in several oxidation states but the most stable and common forms are Cr (0), Cr(III), and Cr(VI) species. Cr toxicity in plants depends on its valence state. Cr (VI) as being highly mobile is toxic, while Cr(III) as less mobile is less toxic. Cr is taken up by plants through carriers of essential ions such as sulphate. Cr uptake, translocation, and accumulation depend on its speciation, which also conditions its toxicity to plants. Symptoms of Cr toxicity in plants are diverse and include decrease of seed germination, reduction of growth, decrease of yield, inhibition of enzymatic activities, impairment of photosynthesis, nutrient and oxidative imbalances and mutagenesis. Chromium may enter the natural waters by weathering of Cr-containing rock, direct discharge from industrial operations, leaching of soils, among others. In the aquatic environment Cr may suffer reduction, oxidation, sorption, desorption, dissolution and precipitation.

The aqueous solubility of Cr (III) is a function of the pH of the water. Under neutral to basic pH Cr (III) will precipitate and conversely under acidic pH it will tend to solubilize, the forms of Cr(VI) chromate and dichromate are extremely soluble under all pH conditions but they can precipitate with divalent cations. The recommended limits for Cr concentration in water are 8 $\mu\text{g L}^{-1}$ for Cr (III) and 1 $\mu\text{g L}^{-1}$ for Cr(VI). In the effluents in the vicinity of Cr industries the levels of Cr range from 2 to 5g L⁻¹.

CHROMIUM:

Chrome has a nice shine, it's impervious to stretches and protects against corrosion – provided that the layer is thick enough and has been professionally applied. Chromium is used to harden steel, to manufacture stainless steel (named as it won't rust) and to produce special alloys. Chromium plating can be used to give a polished mirror finish to steel. Chromium plated car and lorry parts, such as bumpers, were once very common. It is also possible to chrome plate plastics, which are often used in bathroom fittings. About 90% of all leather is tanned using chrome. However, the waste effluent is toxic so alternatives are being investigated. Chromium compounds are used as industrial catalysts and pigments (in bright green, yellow, red and orange colors). Rubies get their red color from chromium, and glass treated with chromium has an emerald green color. Chromium plating, otherwise known as chrome plating, uses the technique of electroplating a fairly thin layer of chromium onto a plastic or metal surface.

- Great surface finish
- Rare to little rising
- Aesthetics

POLLUTION COST BY CHROMIUM:

If the chrome surface is insufficiently polished or rough (not visible to the naked eye), the water doesn't drip off it very well, forming lime scale. When this is scoured off, cracks can ensue – especially on cheap products that have only been coated with a thin layer or where a poorly adhering plastic is on the base. The result is the chrome cracks and/or peels off. So corrosion protection is compromised and rust may form.

Swiss suppliers have invested a lot in recent years to ensure compliance with these regulations – something which however has made the process more expensive. That is why many European-produced fittings are now shipped to China or other distant locations – to be chrome plated and returned. There are less stringent requirements in some of these countries, and items can be processed more cheaply – notwithstanding the costs and the environment.

II. LITERATURE REVIEW

SOLID WASTE AND LIQUID WASTE:

Bradford H. Jones (1976) the authors studied a process disclosed for incinerating tannery waste solids containing organic material and chromium which comprises burning at least one ton per day of said waste in the



combusting zone of a industrial furnace at a low temperature, preferable between at 800 °F and 1200° F to convert at least a portion of the organic material to gases and the chromium to ash, removing the gases from the furnace. The waste solids include sludge separated from liquid waste, leather scrap, or preferable both. By controlling temperature, waste composition, or both, the chromium in the ash can be obtained in either trivalent or hexavalent form. The hexavalent chromium can be extracted with solvent for reuse in the tanning process. Trivalent Chromium, with or without carbons, can be recovered as chromic oxide in an improved stable form for landfill storage or shipment to a reprocessing center.

Changdao Mu, *et al.*, (2003), various alkali and enzymatic hydrolysis were compared, and calcium oxide was found to be important for effective (but still incomplete) hydrolysis. Three Possible reasons are given for the incomplete hydrolysis under alkaline condition. Data for 19 amino acids are presented for four different treatment products.

Kanagaraj *et al.*,(2008) the authors reports in this paper, an attempt has been made to recover the chromium present in spent tan liquor using neutralized wattle extract. The wattle extract at different pH conduction (pH 7,8 and 9) was used for recovery of chromium. The Neutralized wattle extract was made to react with chromium in the spent liquor and allowed to settle for a period of 6 hour. Major amount of chromium settles at the bottom leaving minimal amount in the supernatant. The chrome was recovered and reused for tanning the pelt. The wattle extract that was left in the tanning bath was reused for post tanning process as a retaining agent. Therefore, complete utilization of the chromium and wattle extract has of 85% and 87% (precipitate and supernatant) in experimental leather could be obtained in comparison with the exhaustion of 74% in control sample. The physical strength and color properties of the experimental leather were comparable to the control leather. The overall results show that the recovered chromium can be well used for tanning purpose to obtain the leather of comparable properties.

Determination of the initial chromium content of leather waste:

Firstly, the initial chromium content of waste is determined

- 1) A series of 5 samples were taken dried leather waste shaving (5 g each one)
- 2) The samples was incinerated in a furnace at 600 ± 25 °C
- 3) a Concentrated mixture of HClO_4 (10mL)/ H_2SO_4 (15 ml) is used for oxidizing Cr(III) to Cr (VI) under boiling This conversion was observed by color change from green to orange. The chlorine is totally eliminated by boiling (a negative test when potassium iodide paper is held in the vapor indicates the absence of chloride).
- 4) The obtained solution treated with 10 ml of Potassium iodide (10%) causes the reduction of the hexavalent chromium. The iodine formed being titrated by the sodium thiosulfate solution $\text{Na}_2\text{S}_2\text{O}_3$ (0.1 N) in presence of starch powder as an indicator. Eq (1). The Chromium content was determined by the following expression:
Chromium oxide content (%) - $(A \cdot N \cdot 0.02533 \cdot 100) / Q$ (1)

Where,

A is the milliliters of titrating reagent used,

N is the normality of the titrating reagent

W is the weight of the specimen in grams and 0.02533 is the standard quantity in grams of Cr_2O_3 is titrated by one Milliliter of $\text{Na}_2\text{S}_2\text{O}_3$ (0.1N).

Effect of the alkali concentration:

- ❖ A series of 8 samples were taken dried leather waste shavings (5 g each one)
- ❖ 100ml of distilled water added into the samples.
- ❖ 11.3g potassium tartrate added into the 8 samples.
- ❖ A series of first 4 samples NaOH was adding in different concentration like as, 0.2g, 0.4g, 0.8g, 1g.
- ❖ A series of Next 4 samples Calcium carbonate was adding in different concentration like as, 0.37g, 0.74g, 1.48g, 1.85g.
- ❖ The samples were soaked for 2 days
- ❖ After the samples was filtered by using whatmann 1 Filter paper
- ❖ After filtration the sample was incinerate in a furnace at 600 ± 25 °C
- ❖ Chromium determination from obtained ashes
- ❖ A concentrated mixture of HClO_4 (10 mL)/ H_2SO_4 (15 mL) is used for oxidizing Cr (III) to Cr (VI) under boiling.
- ❖ This conversion was observed by color change from green to orange. The chlorine is totally eliminated by boiling (a negative test when potassium iodide paper is held in the vapor indicates the absence of chlorine).



❖ The obtained solution treated with 10 mL of potassium iodide (10%) causes the reduction of the hexavalent chromium. The iodine formed being titrated by the sodium thiosulfate solution Na₂S₂O₃ (0.1 N) in presence of starch powder as an indicator Eq. (1). The chromium content was determined by the following expression:

$$\text{Chromium oxide content (\%)} = (A \times N \times 0.02533 \times 100) / W \text{---- (1)}$$

Where,

A is the milliliters of titrating reagent used,

N, the normality of the titrating reagent,

W is the weight of the specimen in grams and 0.02533 is the standard quantity in grams of Cr₂O₃ titrated by one milliliter of Na₂S₂O₃ (0.1 N).

III. RESULT AND DISCUSSION

INITIAL CHROMIUM CONTENT IN LEATHER WASTE

A series of 10 samples of dried shavings (5g each one) is incinerated. Firstly, the initial chromium content of waste is determined.

Initial chromium content of experimented waste samples can range from 5/29to 5.50% (Table 1). The average value about 5.50% of chromic acid (Cr₂O₃) close to that given in the literature can be considered as the initial chromium content for all the following experimental parts.

Calculation:

$$1) \text{ Chromium oxide content (\%)} = (A \times N \times 0.02533 \times 100) / W$$

$$= (43.5 \times 0.1 \times 0.02533 \times 100) / 2$$

$$= 5.509$$

$$2) \text{ Chromium oxide content (\%)} = (A \times N \times 0.02533 \times 100) / W$$

$$= (41.7 \times 0.1 \times 0.02533 \times 100) / 2$$

$$= 5.28$$

Table: 1

Initial chromium content of leather waste samples.

Samples	Initial content (%)	Chromium content (%)	Average	Literature content (%)	chromium
0.1	5.50				
0.2	5.28				
0.3	5.04	5.3		5.5	
0.4	5.38				
0.5	5.21				

EFFECT OF THE ALKALI CONCENTRATION

The samples of 5g dried waste leather were treated in different extraction baths constituted of 100mL of distilled water, potassium tartrate 0.05M,0.1M,0.2M,0.25M, and various alkali (NaOH) concentrations: 0. The experimentation was carried out at room temperature during 72h of reaction time. During the treatment, the initial and final pH values of bath were recorded. In parallel, some pilot tests of treatment with various concentrations of NaOH 0.05M, 0.1M, 0.2M, 0.25M, and 5M, in absence of potassium tartrate, in similar conditions as previously were done. At the end of experimentation, the samples were rinsed. Dried and then incinerated. The chromium extraction yields determination



was carried out according to the official method. During treatment, a significant decrease of initial pH value of baths is observed with weak concentrations of alkali (Table 6). Consequently, weak yields of chromium extraction were observed. On account of the progressive alkali concentration increase, the initial pH of the baths tends to be increasingly stabilized and chromium extraction efficiency follows this tendency.

Table 2

Chromium extraction yields according to the alkali concentration. waste was observed, due principally to the strong hydrolysis action of the hydroxyl groups(OH-) on chromium complex sand collagen.

It appears clearly that potassium tartrate plays an important role in the chromium extraction. Its reaction with this latter allows the hydrolysis limitation by the groups OH- (competitive reactions) and the reduction of the ability of the chromium complexes lately formed to condense inside waste. Moreover, it promotes the formation of new more stable chromium complexes, in the light of this fact, the desorption in the baths is much easier, and the chromium extraction efficiency is more important

Calculation:

$$1) \text{ Chromium oxide content (\%)} = (A \times N \times 0.02533 \times 100) / W$$

$$= (21.5 \times 0.1 \times 0.02533 \times 100) / 2$$

$$= 2.72$$

$$2) \text{ Chromium oxide content (\%)} = (A \times N \times 0.02533 \times 100) / W$$

$$= (22.8 \times 0.1 \times 0.02533 \times 100) / 2$$

$$= 2.88$$

Chromium extraction yields according to the alkali concentration.

Tartrate (M)	Concentration Alkali(M)	Concentration content (%)	Residual chromium
	0.1	2.88	
0.5	0.2	2.72	

IV. CONCLUSION

0.5 M potassium tartrate and 0.25M NaOH concentration have been found to be most effective for chromium removal from solid leather waste

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