International Journal of Advance Industrial Engineering
ISSN 2320 –5539

Available at http://inpressco.com/category/ijaie

Research Article

Reduction of Hexavalent Chromium from Chrome Shavings

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Accepted 27 Feb. 2013, Available online 1March 2013, **Vol.1, No.1 (March 2013)**

Abstract

The chrome tanned leather shavings which are produced by chrome tanning process and disposed as a waste, has to be treated and recycled. In this study the chrome shavings were incinerated at 1000^{o}C to transform chromium III to chromium VI. In our previous work on extraction of chromium six from chrome shavings, the dichromate was leached and all the factors affecting leaching were determined, the optimum values of these factor: were solid/liquid ratio of 1:10, time of 1 hour and temperature of 37^{o}C with mixing at 200rpm. The hexavalent chromium was reduced to basic chromium sulphate using 250% water, 92% Sulphuric acid and 25% sugar based on the dichromate weight. The basic chromium sulphate obtained was of 33% basicity and 21% chromic oxide with conversion of 96.80%. Experiments on the reaction kinetics were performed to determine the reaction order, the reaction rate and conversion. These were found to be first-order reaction and 100% conversion after ageing for two weeks. Complete reduction was achieved in three hours with pH of 2.5. A chrome tanning trials were performed using pickled sheep skin. The tannage was completed and the pelts passed the boiling test, then pelt were neutralized and fat-liquored and left overnight. The dried pelts were conditioned and the crusts produced were subjected to chemical and physical analysis, with chromic oxide 4.4, moisture content 14%, ash content 4.6%, shrinkage temperature 100^{o}C, fat content 3.4% , tensile strength 171kg/cm^{2}, elongation at break 49% , tear strength 100kg/cm, and load at grain burst 40 kg.

***Keywords**: Chrome shavings, Hexavalent chrome, Reduction, Solid waste, Leather*

1. Introduction

The chrome tanning process is considered as one of the main processes in the tanning industry in which the raw hides and skins are transferred into leather (ELShaha *et al*., 2010) .Chrome is the most used type of tanning materials (Ludvil, 2002).Chromium (Cr) is a transition metal present in group VI-B of the periodic table. Although it can exists in nine valence states, from −2 to +6 (Smith et al., 2002) only trivalent chromium Cr (III) and hexavalent chromium Cr (VI) are ecologically important because these are the most stable oxidation states in the natural environment. Hexavalent chromium polluted anthropogenic effluents are principally answerable for environmental contamination by toxicity and carcinogenicity. Chromium polluted soils and sediments are usually the result of sewage sludge disposal or dumping of chromate wastes from industrial and manufacturing activities (McGrath and Smith, 1990). Chromium contamination of the environment is of concern because of the mobility and toxicity of Cr (VI). Trivalent and hexavalent chromium differ widely in physicochemical properties and biological reactivity. While Cr (VI) species and dichromate's are extremely water-soluble and mobile in the environment, Cr (III) species are much less soluble and comparatively immobile (Viamajala et al., 2004). Moreover, Cr (VI) is recognized to be highly toxic, carcinogenic, mutagenic and teratogenic for mammals including humans (A. Flores et al., 1999), whereas Cr (III) is an essential trace element necessary for glucose, lipid and amino-acid metabolism as well as a popular dietary supplement (S. Viamajala et al., 2004). Studies have revealed that Cr (VI) is approximately 100 times more toxic (Beszedits, 1988) and 1000 times more mutagenic than Cr (III) (Lofroth et al., 1978).

Currently more than 90% of global leather production of 8 billion sq.ft is produced through chrome tannage (Alebel, 2010). The leather industry is responsible for a large generation of chrome waste during tanning processes (Daniel *et al.*, 2012). Chrome waste in the form of tri or hexavalent from leather processing is of significant environmental problems, it occurs in three forms: liquid waste, solid tanned waste and sludge. During chrome tanning process 75-80% of chromium sulphate absorbs into pelts (Hafiz & Baracat, 2010). Up to 33% of chromium is used for tanning by typical tannery is lost in the solid waste in shavings and trimmings (Jones, 1979). Contamination of soil and groundwater due to chromium six is one of the significant environmental problems to date (kiranmayi *et al.*, 2005). The waste containing

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chromium are classified as class one hazardous waste (Daniel *et al.*, 2012), and chromium six is found to be the third most common pollutant hazardous waste (kiranmayi *et al.*, 2005), therefore they need treatment before disposal. A significant amount of chromium was applied in tanning process, more than seventy percent of these are taken up by the leather while one third of this are removed in shavings. Different methods are used for recovery of chromium, including solvent extraction, precipitation, ion exchange and liquid membranes (Samreen *et al.*, 2006). Among the different oxidation states of chromium, Cr (VI) is acutely toxic and carcinogenic. The Cr (III) ion on the other hand has a high tendency to form strong complexes with soil minerals. Incineration of chromium III to chromium VI and its reduction back to basic chromium sulphate is considered to be an important step towards overcoming chromium pollution (kiranmayi *et al.*, 2005). Recently, the *extraction* of chromium six from chrome shavings has been established (Salma et al., 2013). In this study the basic chromium sulphate liquor which was reduced from sodium dichromate was used for tanning pickled sheep skin pelts. The chrome tanned pelts were retanned, dried and made into crust. The crust was subjected to chemical and physical analysis.

2. Materials and Methods

Reduction of Sodium Dichromate to Basic Chromium Sulphate

250 g of sodium dichromate were mixed with 625 g water in a beaker**;** 230 g of concentrated sulphuric acid (Sp. Gr. 1.84) were added carefully and stirred well. The beaker was placed in a reactor under cooling with continuous stirring while 62.5 g of sugar were added slowly in 10 lots over three hours. During the reaction the colour of the liquor changed gradually from orange to green and finally to bluish green indicating the completion of the reduction (Sarkar, 2005). The reaction proceeded as follows:

$4Na_2Cr_2O_7 + 12H_2SO_4 + C_6H_{12}O_6 + 26H_2O = 8Cr(OH)SO_4 + 4Na_2SO_4 + 40H_2O + 6CO_2$ (1)

Test for Complete Reduction

Three drops of reduced chrome liquor were taken in a beaker, diluted with distilled water, ammonia was then added and the mixture was boiled and filtered. No yellow colour was observed in the filtrate indicating complete reduction.

Determination of Chromic Oxide

25 ml of the chrome liquor was transferred into a conical flask and diluted with 100 ml distilled water. 2N caustic soda solution was added drop by drop until the precipitated chromium hydroxide formed was just dissolved. 25 ml of hydrogen peroxide solution (3%) was added. Some boiling stones were then introduced into the vessel and the contents were allowed to boil. A small funnel was suspended in the neck of the conical flask to avoid any loss due to bubbling. The boiled solution (yellow chromate) was cooled and made up to the mark.
50 ml of the yellow chromate solution was pipetted into an iodine flask to which concentrated hydrochloric acid was added in excess (5 ml excess) , followed immediately by 10 ml of 10% potassium iodide, the closed flask was left in a dark for 10 minutes. The liberated iodine was titrated with 0.1 N sodium thiosulphate using freshly prepared starch as indicator; the disappearance of the blue colour indicated the end point.

1 ml of 0.1 N sodiumthiosulphate = 2.533 mg chromic oxide______________ (2)

Determination of Basicity

3 ml of 1% phenolphthalein s olution was added to 300 ml distilled water in a large porcelain bowel and adjusted to pink colour with three drops of 0.1 N sodium hydroxide solution. 25 ml of solution was prepared as described above and titrated with continuous stirring at the boil to effect further hydrolysis of the chromium salt, with 0.1 N sodium hydroxide until the distinct pink colouration was obtained.
Bacisity = A-B / A× 100
____ (3)
A = ml of 0.1 sodium thiosulphate.
B = ml of 0.1 sodium hydroxide.

Table I Recipe for chrome tannage, percentage was based on pickled pelt weight.
Cr_2O_3: 21%, Basicty: 33%

Material	%	Quantity kg	Duration min	Remarks
Float	100	15	30	
Reduced chrome liquor	10	1.5	240 left overnight	pH 2.8
Sodium bicarbonate	1	0.15	120	pH 5.5 piled 24 hours
Mimosa	10	1.5	240	
Syntan	10	1.5	240 left overnight	
Fatliquor	5	0.75	240	Paste-dried

Conversion of Sodium Dichromate to Basic Chromium Sulphate

Sulphuric acid was used in the reaction of sodium dichromate with sugar to produce basic chromium sulphate. Sugar was used as a reducing agent; the reaction was as shown in equation 1

The conversion was = 250 – 8 / 250 × 100 = 96.8%
Where:
250 gm of dichromate was used.
8 gm of dichromate was left unreacted.

Tanning process

Pickled sheep skins (15 kg) were tanned using the reduced basic chromium sulphate, obtained by the mentioned process (**Table I**).

3. Results and Discussion

Basic chromium sulphate was produced gradually over three hours. To measure the reaction rate, a sample of the chrome liquor was taken every 10 minutes until complete reduction. The concentration of the chrome liquor as chromic oxide was determined using the hydrometer (baume). The composition was obtained using a calibration chart as shown in figure 1. This calibration chart was determined using chromsal B.

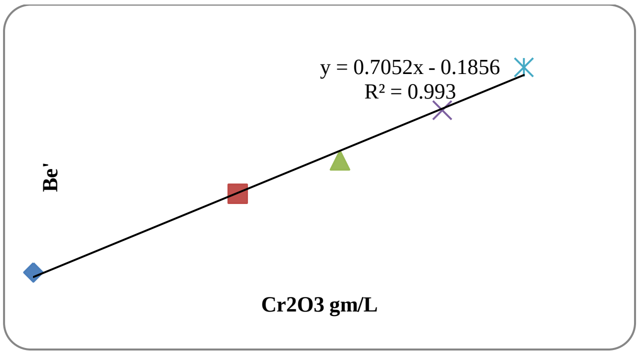

Fig. 1: Calibration and correlation of chromic oxide Vs degree baume

In the process of reduction the chromic acid mixture yielded oxygen that oxidized the reducing agent ($C_6H_{12}O_6$) producing (CO_3) and the hexavalent chrome in the form of CrO_3 in the dichromate was reduced to trivalent form as follows

$$12CrO_3+C_6H_{12}O_6 \rightarrow 6Cr_2O_3+6\,CO_3+ 6H_2O \quad (4)$$

The chromic oxide thus formed combined with concentrated H_2SO_4 to produce basic chromium sulphate ($Cr_2(OH)_2SO_4$) of 33% basicity.

$$Cr_2O_3 + 2H_2SO_4 \rightarrow 2Cr(OH)SO_4 + H_2O \quad (5)$$

The conversion was found to be 96.8% indicating that 3.2% of chromium six was left in the liquor of basic chromium sulphate, to raise the conversion from 96.8% to 100% the chrome liquor was aged for two weeks and the chromic oxide was measured every week. The result was that 100% conversion was obtained, and hence no chromium VI was found in the produced basic chromium sulphate.

Hence ageing is very important due to the environmental effect of chromium VI produced in the process of reduction. Therefore the reduction- oxidation reaction should be carefully observed to be free from chromium VI as chromium six is toxic and carcinogenic. It is found that ageing of the basic chromium sulphate liquor completed the conversion to 100 % therefore eliminating the presence of chromium six.

The result from the process of reduction gave the best percentage basicity and chromic oxide which is acceptable compared with the usual concentration.

Chemical analysis

Shrinkage temperature, chromic oxide, total ash, moisture and fat content were measured using standard method (Official methods, 1996), and the results showed acceptable properties compared with standard results as shown in **Table II**.

Table II Chemical analysis of the crust leathers

Item	Contents
Chromic oxide%	4.4
Total Ash %	4.6
Moisture %	14
Shrinkage temperature ^oC	100
Fat and oils%	3.4

Physical analysis

Samples for physical testing were cut and conditioned as per the official methods of analysis (Official methods, 1996), temperature of 20 ± 2^oC and relative humidity of 65 ± 2 for 48 hours. The physical properties of the crust leathers were measured as shown in **Table III**. The physical testing results showed that the method of reduction was 100% conversion.

Table III Physical analysis the crust leathers

Item	Contents	Standards
Tensile strength(kg/cm^2)	171	150
Elongation (%)	49	20-50
Tear strength (kg/cm)	100	80
Load at grain burst (kg)	40	20

Conclusion

Chromium is normally nontoxic in the trivalent state, but the research studies indicate the oxidation of the trivalent chromium to the hexavalent state, that is recognized to be highly toxic, carcinogenic, mutagenic and teratogenic for mammals including humans. Chromium is a valuable resource and its extraction and reuse is economical and environmentally feasible. In the present study, it is seen that the reduction of chromium VI to chromium III is the better way for protecting the environment from the contamination with hexavalent chromium. The completion of reducing dichromate through ageing showed no appearance of chromium VI in the basic chromium sulphate produced. The reducing agent i.e., sugar, can be replaced with molasses from sugar cane industry, which is cheaper and available.

Also in the present study, an attempt has been made to produce upper leather using tanning process based on reduced chrome liquor. It is seen that tanning system with reduced chrome liquor resulted in leathers with shrinkage temperature of 100^0C.

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