



Production of basic chromium sulfate by using recovered chromium from ashes of thermally treated leather

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ABSTRACT

Leather wastes tanned with chromium are generated during the production process of leather, hence the wastes from hand crafted goods and footwear industries are a serious environmental problem. The thermal treatment of leather wastes can be one of the treatment options because the wastes are rich in chromium and can be used as a raw material for sodium chromate production and further to obtain several chromium compounds. The objective of this study was to utilize the chromium from leather wastes via basic chromium sulfate production to be subsequently applied in a hide tanning. The obtained results have shown that this is the first successful attempt to achieve desired base properties of the product. The result was achieved when the following conditions were applied: a molar ratio between sodium sulfite and sodium dichromate equal to 6; reaction time equal to 5 min before addition of sulfuric acid; pH of sodium dichromate solution equal to 2.

Summarizing, there is an opportunity to utilize the dangerous wastes and reused them in the production scheme by minimizing or annulling the environmental impact and to attend a sustainable process development concept.

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1. Introduction

The activities related to leather and footwear industry processes have a high impact on the environment due to the high quantity of process residues. The wastes are classified as dangerous by the Brazilian Legislation, mainly due to the presence of chromium. Moreover, effluents and pollutants are generated from different sources (gases, liquids and solids) during the multi-step leather process.

The disposal of these residues is a concern because their accumulation in the environment has increased during the years. The search of alternatives for re-use, recycling, treatment and correct disposal has been the focus of much research.

According to Vieira [1], approximately 300 tons per day of wastes containing shavings of leather are generated in Brazil. One of the alternatives to utilize these wastes is the thermal treatment. The ashes formed in the process can be used as a raw material to obtain sodium chromate, which is the production precursor of a basic chromium sulfate (BCS), salt widely used in the hide tanning. Due to a high concentration of chromium oxide (between 40 and

50% of Cr₂O₃) in the ashes obtained after the thermal treatment, this material can be used as a chromite substitute. It is desirable to recover chromium ashes and reused them in the leather tanning process, through a basic chromium sulfate.

The basic chromium sulfate production includes a step of hexavalent chromium reduction. According to Udy [2], a careful acidity adjustment, dilution (concentration) and molar ratio between reduction agent and dichromate are important variables of a basic chromium sulfate production process, where the final product may reach excellent tanning characteristics.

Basicity is considered a determinant feature of basic chromium sulfate with an excellent tanning power. The basicity indicates the number of hydroxyl radicals attached to the chromium atom. An increase of basicity decreases the diffusion of salt, but increases the fixation to the hide. There are salts with different basicities in the market such as 33%, 40%, 48% and 50%, respectively. The most utilized chromium salts in hide tanning have basicity of 33% or less, in order to guarantee the optimal chromium diffusion into the material and to avoid a superficial tanning.

According to Covington [3], the basic chromium sulfate with basicity 33% has pH in solution about 2.8 and contains mostly bi-nuclear species, while the basic chromium sulfate solution with basicity 50% has pH about 3.5 and contains tri-nuclear species.

In the work of Hoinacki et al. [4] to reduce chromium(VI) to its less mobile and toxic chromium(III) form, several reduction agents

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such as – sucrose, glucose, glycerin, molasses, sulfur dioxide, bisulfite, thio-sulfate, and sodium sulfite were used. The reaction occurs usually in the presence of sulfuric acid.

The authors Erdem and Tümen [5] carried out the chromium reduction with sodium sulfite. First, Cr(VI) solution in the concentration of 200 mg Cr(VI)/l was prepared by dissolving $K_2Cr_2O_7$ in distilled water. The pH of this solution was adjusted to 2 ± 0.1 by a H_2SO_4 solution. A stoichiometric amount of sodium sulfite, was added to this solution and the Cr(VI) was reduced by shaking the mixture for a period of 15 min.

In addition, a second solution of Cr(VI) was prepared in the same way by using ferrous sulfate as reducing agent. It has been reported that an excess dosage of the theoretical amount of ferrous sulfate (approximately 2.5-fold) is required to obtain complete reduction of Cr(VI) in a short period of time.

During the reduction reaction, the quantity of used acid can vary. It depends on the desired final chromium sulfate basicity [2]. According to Hoinacki [6], the resulting solution basicity is related to the acid amount used in the reduction reaction. As much acid was added as lower the obtained solution basicity was.

After the thermal treatment of ashes chromate, Pereira [7] tested the glucose and sulfuric acid components to obtain a basic chromium sulfate. The obtained solutions presented basicity between 40 and 50%.

Erdem [8] studied the chromium recovery conditions in the form of soluble chromate from chrome shaving by oxidation with air, oxygen and Na_2O_2 . The chromate ions in the solution were reduced by using Na_2SO_3 , and Cr(III) sulfate solution was obtained. For this purpose, pH of the solution was adjusted to 2 ± 0.1 by using H_2SO_4 solution and a stoichiometric amount of Na_2SO_3 was added. Chromate ions in the solution were reduced at the end of contact period of 30 min, and chrome sulfate solution was obtained. When this solution is basified by adding a basification agent such as sodium hydrogen carbonate, it can be reused as tannage in tanning.

Hence, the principal aim of the present work was to study the process of basic chromium sulfate production with basicity similar to that of the commercial product, because the basicity characteristic was a fundamental one for chromium salts tanning procedure. In order to achieve this goal we have used both sodium sulfite and sulfuric acid in the chromium(VI) reduction process.

2. Materials and methods

2.1. Materials

The sodium chromate used in this study as a raw material for production of basic chromium sulfate was previously produced according to Dettmer et al. [9]. The other reagents were of analytic purity grade.

2.2. Process of basic chromium sulfate production

The initial tests were performed by using 100 mL sodium chromate obtained from the ashes of thermal treatment. In previously work, chromium oxidation (recuperation) was found to be about 94% [9], so most of chromium in ashes is recovered in the form of sodium chromate and could be used in basic chromium sulfate production.

The solution used for obtain basic chromium sulfate had concentration between 1.20 and 1.55 g Cr_2O_3 /l. The chromium concentration in the sodium chromate solution was calculated according to the conversion of trivalent chromium(III) to hexavalent chromium(VI) in the oxidation reaction published elsewhere

[9]. The chromium oxidation [$u(\%)$] was calculated as follows:

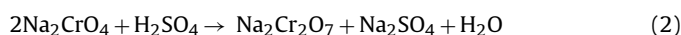
$$u(\%) = \left(1 - \frac{Cr_f}{Cr_i}\right) \times 100 \quad (1)$$

where $[Cr_f]$ is the final fraction of chromium oxide in residue (filter); $[Cr_i]$ is the initial fraction of chromium oxide in ashes.

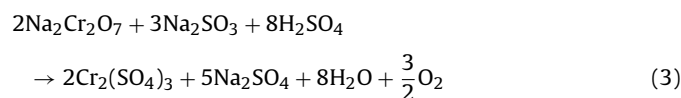
The concentrations $[Cr_i]$ and $[Cr_f]$ were determined according to ASTM D 2807-93 (1998). The results were compared with the ones obtained by applying atomic absorption analysis and the conclusion was that both analytical techniques show similar results.

Sodium chromate solutions with similar oxidation strength and dilution were used for all experiments. The pH of solution was controlled by addition of sulfuric acid in favor of a sodium dichromate formation. The pH of sodium dichromate solution was monitored, as well.

The forward reaction of sodium dichromate formation can be written as follows



The forward chromium(VI) reduction reaction is presented by Eq. (3)



Note: Sodium sulfite was added in a balloon, and then the sodium dichromate solution was added. The process time of sodium sulfite and sodium dichromate reaction was predetermined. Further, sulfuric acid was added to complete the chromium reduction process. Reagents, sodium sulfite and sulfuric acid were used in excess. Because the completion of the reaction is not quantitatively possible, a qualitative test for chromium(VI) determination was performed as follows: 5 drops of solution (from balloon) were added into a test tube, where 2 drops of HNO_3 (3 M), 20 drops of ethyl ether and 3 drops of H_2O_2 (3%) were placed. The mixture was agitated, and a blue color of the ether layer indicated the presence of sodium chromate. Sulfuric acid was quantitatively added until the ether layer became colorless [7]. When the chromium reduction was confirmed through the described test, its product was placed in a Becker and the pH of solution was monitored.

The pH adjustment of the chromium sulfate solution was carried out by using sodium hydroxide or sodium bicarbonate and as a reference a commercial basic chromium sulfate solution (33% basicity and 26% chromium oxide) was used.

The basicity (BC) of basic chromium sulfate solution was measured according to ASTM 3897-93 [10], and the quantity of chromium oxide (Cr_2O_3) was determined according to ABNT NBR 13.341 [11] or ASTM 3898-93 [12].

The investigated process parameters were chosen as follows: molar ratio between sodium sulfite and sodium dichromate (RM); pH, reaction time (t); and alkali used for pH adjustment (B). All experiments were made in duplicate.

2.2.1. Molar ratio between sodium sulfite and sodium dichromate

As a first step, the molar ratio between sodium sulfite and sodium dichromate on the hexavalent chromium(VI) reduction process was defined. Three different molar ratios between the reactants were evaluated. The principal aim was to obtain efficient chromium reduction and ideal product basicity (33%). The reaction time ($t=5$ min) and the pH of dichromate solution (pH=2) were controlled. The obtained ashes from thermal treatment of footwear industries wastes contain impurities which can be extracted in the sodium chromate solution, thus an excess of sodium sulfite was necessary in order to keep the reaction stoichiometry.

2.2.2. pH and time

The experiments were carried out to find the optimal pH of dichromate solution, which corresponded to a chromium sulfate solution basicity close to 33%. The influence of process time of sodium sulfite and sodium dichromate reaction before an acid addition were investigated as well.

2.2.3. Alkalis

The alkali influence (used for pH adjusting) on sulfate basicity was investigated. For the pH adjustment of basic chromium sulfate solution in lab scale, sodium bicarbonate and sodium hydroxide were used, where the molar ratio between sodium sulfite and sodium dichromate was fixed at 6, the reaction time before the acid addition was 5 min, and the sodium dichromate solution pH was equal to 2.

3. Results and discussion

3.1. Process for basic chromium sulfate production

The results on a basic chromium sulfate production process are presented below. For all tables, the results have shown basicity and chromium oxide concentration profile as a function of process variables.

3.1.1. Molar ratio between sodium sulfite and sodium dichromate

Table 1 shows the results for different molar ratio values. Note that the stoichiometric molar ratio between sodium sulfite and sodium dichromate is equal to 1.5.

For the experiments 1 and 2 it was impossible to evaluate the compounds basicity because no complete reduction of chromium(VI) was observed even after the addition of considerable quantities of sulfuric acid above stoichiometric value. When only sodium sulfite was added, the solutions 1 and 2 were colored in yellow, which is an indication for chromium(VI) presence. Further addition of sulfuric acid did not change the yellow color. Note: The ether layer of both solutions was blue colored, when qualitative test of chromium(VI) was carried out. The solution 3 was colored green-yellow when sodium sulfite was added. This was an indication of increased reduction of hexavalent chromium as a function of molar ratio changes. Further, an addition of sulfuric acid resulted in a colorless ether layer, confirming a complete reduction of chromium(VI).

The obtained product basicity for the molar ratio 6 is in accordance with the one of the commercial salt which is equal to 33%.

Table 1

Basicity (BC) of chromium compound obtained with different molar ratios between sodium sulfite and sodium dichromate. Controlled variables: t (min) = 5, pH = 2, alkali (B) = NaOH.

Exp.	RM (mol/mol)	$C_{Cr_2O_3}$ (g/l)	BC (%)
1	1.5	–	–
2	3	–	–
3	6	1.52	33.17

Table 2

Basicity (BC) as a function of pH, sodium dichromate concentration and reaction time changes. Controlled variables: RM (mol/mol) = 6, alkali (B) = NaOH.

Exp.	t (min)	pH	$C_{Cr_2O_3}$ (g/l)	BC (%)
1	5	1	1.63	21.10
2	5	2	1.52	33.17
3	5	3	1.39	17.05
4	15	1	1.30	18.50
5	15	2	1.44	28.43
6	15	3	1.17	27.50
7	30	2	1.45	48.50

Table 3

Basicity values obtained when different basic compounds were used. Controlled variables: RM (mol/mol) = 6, t (min) = 5, pH = 2.

Exp.	B	$C_{Cr_2O_3}$ (g/l)	BC (%)
1	NaHCO ₃	1.55	33.50
2	NaOH	1.52	33.17

3.1.2. pH and time

Table 2 presents set of experiments when the controlled variables were changed in order to find the optimal basicity value of the product.

The results have shown that basicity value were close to the desired (33%) value when the pH value of sodium dichromate was equal to 2, and reaction time was in the range from 5 to 15 min. Satisfactory values were obtained for pH = 3 and reaction time 15 min.

The basicity variation from the optimal value can be addressed to the sulfuric acid addition. The longer reaction time between sodium sulfite and sodium dichromate solution, cause higher hexavalent chromium reduction. Hence, a small quantity of sulfuric acid was necessary to add for completion of the reduction reaction, which has influenced the final compound basicity, as well. The resulting solution basicity is related to the acid amount used in the reduction reaction. Studies on Cr(VI) reduction has reported that the efficiency of reducing agent depends largely on amount of acid and reduction reaction rapidly occurs at low pHs [13–15].

3.1.3. Alkalis

To verify the influence of different alkalis compounds on chromium compound basicity, the set of experiments with addition of sodium hydroxide and sodium bicarbonate were performed (see Table 3).

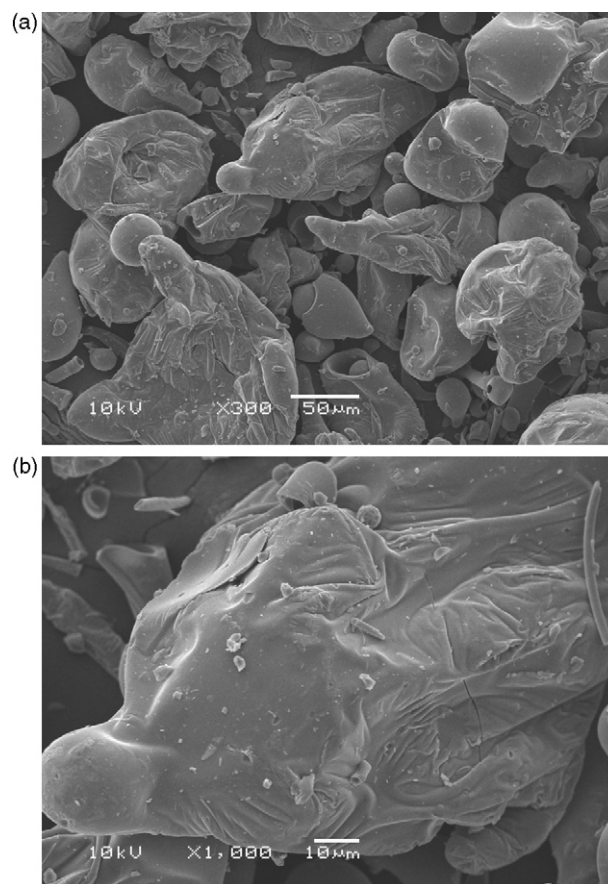


Fig. 1. SEM of commercial basic chromium sulfate sample with magnification of (a) 300 \times and (b) 1000 \times .

Analysis of the results have shown that both compounds can be used to obtain optimal (33%) basicity of the product. Hence, a further utilization of one or another compound will exclusively depend on the economical evaluation of the process. It can be noted as well, that when sodium bicarbonate is used, a higher quantity of the reagent is necessary for pH adjustment which may cause an unfavorable increasing of mineral salts in the BCS solution. Further, the quantity of ashes in the leather tanned procedure might not be in accordance with the standard.

3.2. Basic chromium sulfate characterization

The commercial and lab product samples were electronically scanned by using an X-ray diffraction. Figs. 1 and 2 present the scanning electronic microscopy (SEM) for the commercial basic chromium sulfate and the lab product samples.

In Figs. 1 and 2, one can see that the commercial basic chromium sulfate and laboratory samples present different surfaces. The commercial product possesses flat surface with no porosity, when the product obtained in the laboratory has a rough surface, which could be due to a deposition of salts as a result from sodium bicarbonate excess.

In Figs. 3 and 4 X-ray diffractions of the commercial and laboratory product samples are shown.

Analysis of Fig. 3 showed that there were no peaks in the studied product which can be interpreted that no crystalline form of solids was involved. Thus, BCS can be considered as an amorphous material.

In the product synthesized in laboratory, the presence of BCS was not detected which suggested that the structure of this product

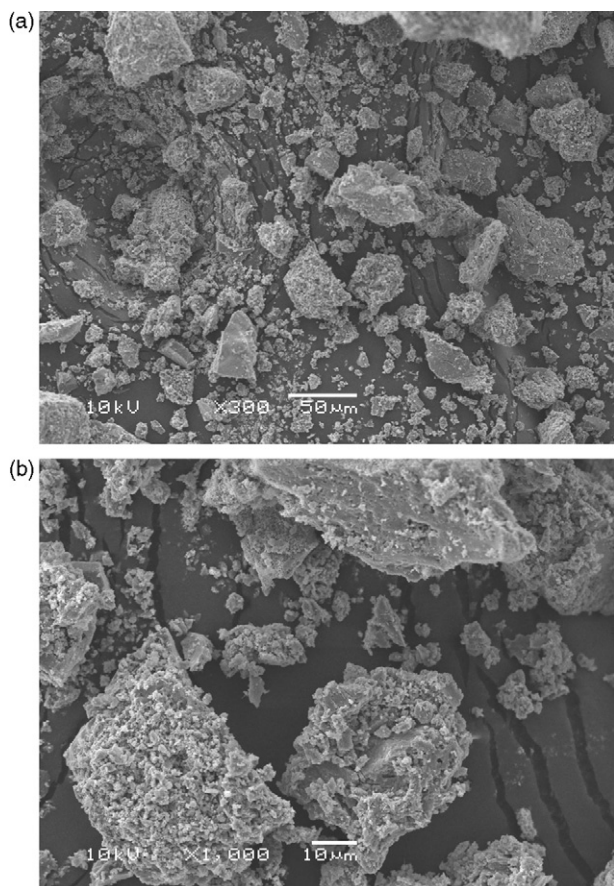


Fig. 2. SEM of lab basic chromium sulfate sample, with magnification of (a) 300× and (b) 1000×.

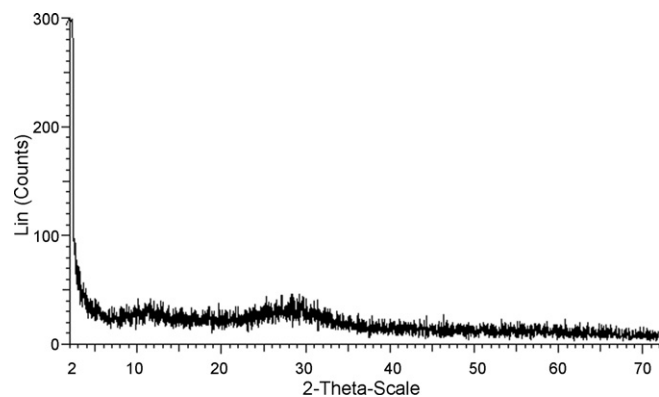


Fig. 3. X-rays analysis of commercial basic chromium sulfate sample.

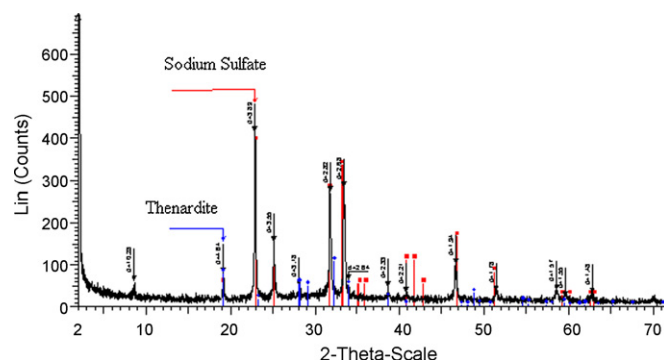


Fig. 4. X-rays analysis of basic chromium sulfate obtained from the ashes in the lab conditions.

was amorphous, as well. However, sodium sulfate and thenardite (other sodium sulfate compound) were identified. These compounds are formed during the sodium dichromate formation and during reduction reaction of hexavalent chromium(VI) (see Eqs. (2) and (3)).

4. Conclusions

The results obtained in this study have shown a possibility to produce chromium sulfate from recovered chromium from leather wastes ashes by applying thermal treatment and to reuse it in hide tanning. The most important achievement of this work was that the obtained tanning salt had similar basicity properties compared with that of the commercial product. Analyzing the previously published works in the field ([7,16–18]), it should be noticed that this is the first successful attempt to obtain desired base properties of the product. The result was achieved when applied the following conditions: a molar ratio between sodium sulfite and sodium dichromate equals to 6; reaction time equals to 5 min before addition of sulfuric acid; pH of sodium dichromate solution equals to 2, and solution pH adjustment by using sodium hydroxide. Because the wastes are classified as environmentally harmful, further studies are needed in order to guarantee the required product properties in an industrial scale where a re-use of the product will result in a minimization of the environmental impact and a contribution for sustainable process development.

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