

Leaching behavior of chromium in chrome shaving generated in tanning process and its stabilization

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Abstract

In this study, leaching properties and pollution potential of chromium in chrome shaving (CS), which is a solid residue of leather industry, containing 2.27% Cr were investigated and thermal stabilization procedure was applied to the CS for chromium immobilization. For this purpose, firstly, effects of the liquid/solid ratio, contact time, pH and sequential extraction on the leaching behavior of chromium in the CS were studied. It was determined that the CS-caused chromium pollution is a hazardous material for environment. Thermal stabilization procedure was applied to the CS in the temperature range of 250–500 °C for the chromium immobilization. Effective stabilization of chromium in the CS was achieved by heating of CS at 350 °C under CO₂ atmosphere. Leaching experiments were also carried out with the samples obtained from the stabilization process and the results compared with that of the CS. Also, TCLP test method was applied to the samples to determine pollution potentials and discharge situations of the CS and its stabilization products. While the chromium concentrations in the test solutions of all samples stabilized thermally at above 350 °C were below the USEPA regulatory limit of 5 mg/l, the concentration of chromium leached out from the CS was 30-fold bigger than the USEPA regulatory limit.

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1. Introduction

Protein- and chemical-based solid wastes and liquid wastes generate in the leather industry. Among these wastes, chemical-based solid wastes generate in tanning process. Skin in tanning process, which is the main process that protects leather against some environmental effects such as microbial degradation, heat, sweat or moisture, etc. is stabilized by using a tannage material such as some minerals and vegetable-based substances and aldehyde.

While the skin is stabilized in the process, much greater quantities of by-product and wastes than leather produced generate. One tonne of wet hide yields only 200 kg of leather but over 600 kg of solid waste or by-product [1]. It has been stated that about 600,000 tonnes of solid waste each year worldwide generate by leather industry and approximately 40–50% of the hides are lose to shavings and trimmings [2]. Important quantities of

the chemicals used in the tanning process together hides remain in the solid and liquid wastes. Basic Cr(III) sulphate among the mineral-based tannages is widely used tannage material. When this compound is used as tannage, only 60% of the total chromium reacts with the hides and about 40% of the chromium remains in the solid waste and spent tanning solutions [3]. Also, chrome shavings (CS) constitute 75% of the solid wastes containing chromium in the tanning process. About 0.8 million tonnes of CS could be generated per year worldwide [4]. CS are small particles and mainly consisting of collagen cross-linked with Cr(III) complexes. This waste is partly used in the manufacture of leather board, but most are generally disposed off in landfills or incinerated for elimination of organic residues and reduction of volume of it [4]. In the case of the incineration of these wastes in the air atmosphere, the gases and soluble toxic chemicals, particularly Cr(VI), generate and can cause serious environmental problems such as air, soil and water pollution [5–7].

When taking into consideration amount of the wastes generated in the chromium tanning, it can be stated that the waste management is the most important issue. In the case of direct

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discharge of these wastes, the chromium can dissolve and causes water pollution. In order to examine this situation, in this study, some parameters such as liquid/solid ratio, contact time, pH and sequential extraction affected leaching behavior of chromium in the CS were studied and thermal stabilization procedure was applied to the CS for chromium immobilization. The results were evaluated in order to determine if the CS and its stabilized products can be disposed off at a landfill site with domestic waste by applying the toxicity characteristics leaching procedure (TCLP).

2. Materials and methods

2.1. Materials

CS used in this study was supplied from a Leather Plant in Elazığ (Turkiye). Fresh CS were dried at room temperature for 3 days prior to use in the experiments. The CS was analyzed for ash, chromium, calcium, natrium, TKN and fat based on weight of dry waste. The physical and chemical characteristics of the sample were analyzed according to standard methods [8]. The results are presented in Table 1.

As can be seen in table, chromium is not the only compound present in tannery wastes. As leather undergoes several different treatments, other chemical compounds could be present. Results show that the CS has a significant concentration of sodium (73.6 g/kg) and calcium (7.38 g/kg). This can be explained by the use of some chemical products such as sodium chloride and lime in tanning process.

2.2. Experimental procedure

Experimental study was organized in two different groups. In the first group experiments, leaching properties and pollution potential of the chromium in the CS were determined. In the second group experiment, thermal stabilization process was applied to the CS for immobilization of chromium and pollution potentials of the stabilization products and leaching behavior of the chromium in them were studied.

2.2.1. Leaching properties and pollution potential of chromium in the CS

In order to determine leaching behavior of the chromium, the experiments were carried out in the batch reactors (250-ml erlenmeyer) containing various amounts of CS and 100 ml of solutions having different pHs. The batch reactors were shaken

at 150 rev/min by using a flask shaker (Gallenkamp) for contact times ranging from 15 min to 24 h. All of the experiments were carried out at 25 °C.

At the end of each contact period, the mixtures were filtered and then the final pH of the filtrates was measured by a pH meter. The filtrates were acidified with 1 ml of HNO₃ solution to prevent the precipitation of chromium and then they were analyzed for chromium.

In order to determine pollution potentials of the CS and its products stabilized, the toxicity characteristics leaching procedure (TCLP) was also applied to them. TCLP is widely used to measure leachability and to decide if the treated waste can be landfilled since it is regulatory test for land disposal of wastes. For this purpose, 100 g of samples were placed separately in a plastic bottle together with 2000 ml of leach solution and sodium acetate/acetic acid buffer solution. The mixtures were then agitated at 30 ± 2 rpm and 22 ± 3 °C for 18 ± 2 h. The mixture was filtered through a 0.45-µm glass fibre filter and the filtrates were analyzed for chromium [9].

The experiments were performed in duplicate and mean values were taken into account.

2.2.2. Stabilization of CS

In order to stabilize chromium in the CS, thermal stabilization process was applied. For this purpose, dried CS of 20 g was placed in a reactor and heated in a muffle furnace under the CO₂ atmosphere at different temperatures for 60 min (Fig. 1).

2.3. Methods of analysis

The concentrations of total chromium and calcium in the solutions were determined by atomic absorption spectrophotometer (Ati-Unicam 929). In order to determine the hexavalent chromium content of the extracts, they were analyzed colorimetrically with 1.5-diphenyl carbazide method by using Jenway 6105 Spectrophotometer [10].

In order to determine mineralogical compositions of the samples obtained at various temperatures, the samples were subjected to XRD analysis (Siemens, D-5000).

Table 1
Physical and chemical characteristics of the CS used in the experiments

Parameter	Value
Moisture	57%
Ash	4.75%
Fat	1.45%
TKN	13.82%
Cr	2.27%
Ca	7.38 g/kg
Na	73.6 g/kg

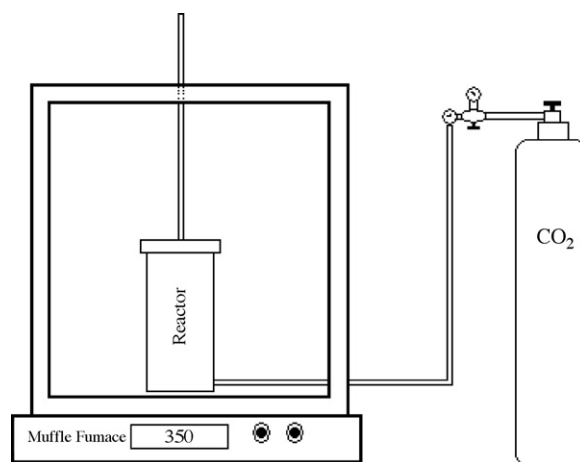


Fig. 1. Schematic diagram of experimental set.

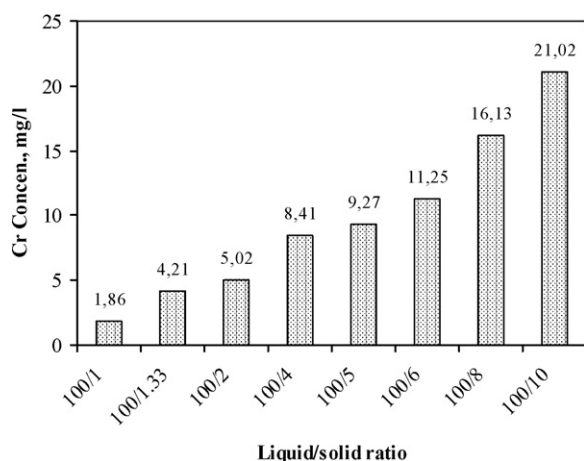


Fig. 2. The effect of liquid/solid ratio on the dissolution of chromium in the CS (contact time: 120 min; temperature: 25 °C).

Standard solutions were prepared by using analytical chemicals. All dilutions were made by distilled water.

3. Results and discussion

3.1. Leaching properties and pollution potential of the chromium in CS

3.1.1. Effect of liquid/solid (L/S) ratio

The L/S ratio is an important parameter needs to be optimized in order to get the correct results and compare them to the standard test methods. Influence of L/S ratio on the dissolution of chromium in the CS was investigated in the L/S ratio range of 10–100. The obtained results are presented in Fig. 2. It is seen from the figure that the chromium concentration in the solution is increased with the decreased ratio of L/S. The chromium concentrations dissolved from the CS at L/S ratio of higher than 50 were above the maximum allowable concentration limit given as 5 mg/l by USEPA. This situation means that the CS is a pollutant when it contacts with water at L/S ratio of higher than 50.

Further experiments were carried out at L/S ratio of 20 to compare the results with the TCLP test method.

3.1.2. Effect of contact time

Fig. 3 shows the effect of contact time on the chromium dissolution from the CS. As seen from the figure, the chromium concentration mostly increases with the increasing contact time and exceeds the allowable concentration limit after 60 min. When the CS contacts with water and/or aqueous solutions, it has been observed that the volume of CS was increased and its texture was softened by water absorption. This situation increases with the increasing contact time and probably causes higher chromium releasing. Consequently, the CS has definitely not contact with water/or aqueous solution for contact time of higher than 60 min.

3.1.3. Effect of pH

Effect of pH on the chromium dissolution from the CS was investigated in the pH range of 3–11. The results showed

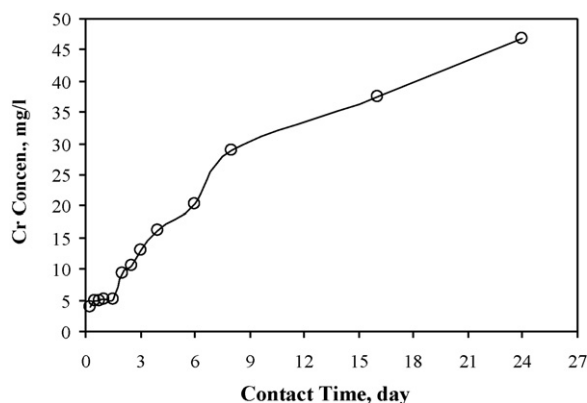


Fig. 3. The effect of contact time on the dissolution of chromium in the CS (liquid/solid ratio: 20; temperature: 25 °C).

that the concentration of chromium released was not significantly affected by the pH and it was changed in the range of 11.2–12.4 mg/l (Fig. 4). Therefore, it has been stated that the pH does not affect the chromium dissolution from the CS.

3.1.4. Effect of sequential extraction

In order to determine effect of the sequential extraction on the chromium dissolution from the CS, a certain amount of CS was subjected to successive extractions. For this purpose, a 5 g of CS and 100 ml of water were mixed and mixture was shaken for 120 min. After each contact time of 120 min, extract was separated from the mixture and new 100 ml of water was added again to the same solid sample and procedure was repeated until the concentration of chromium released into water dropped at lower than 2 mg/l.

It was determined that the chromium concentration released after fourth extraction decreased from 12.44 to 3.52 mg/l and it was found to be under the detection limit after fifth extraction. However, it was observed that important amount of chromium redissolved from the CS dried at room temperature for 2 days. Therefore, the successive extraction was systematically repeated to investigate this situation. For this purpose, the solid extraction residue was dried for 2 days after each extraction period and extractions were carried out under the same conditions mentioned above. The results obtained are presented in Table 2.

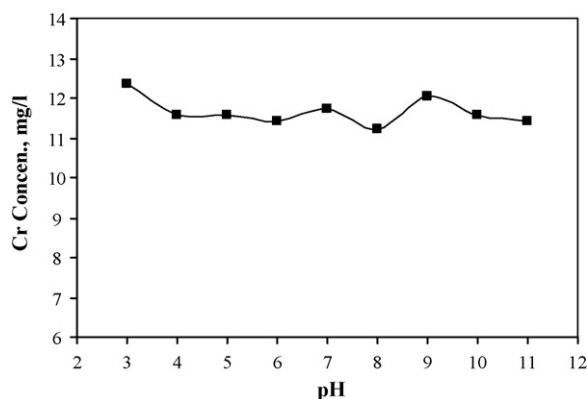


Fig. 4. The effect of pH on the dissolution of chromium in the CS (liquid/solid ratio: 20; contact time: 120 min; temperature: 25 °C).

Table 2
Successive extraction results (liquid/solid ratio: 20; contact time: 120 min; temperature: 25 °C)

Day	Extraction	Released Cr concentration (mg/l)	Cumulative amount of chromium released (mg)
1	1	12.44	1.244
	2	8.12	2.056
	3	5.38	2.594
	4	3.52	2.946
	5	UDL ^a	2.946
3	1	23.7	5.316
	2	4.61	5.777
	3	3.57	6.134
	4	1.5	6.284
5	1	9.55	7.239
	2	1.94	7.433
	3	UDL ^a	7.433
7	1	5.73	8.006
	2	0.5	8.506
	3	UDL ^a	8.506
9	1	4.15	8.921
	2	UDL ^a	8.921
11	1	3.86	9.307
	2	UDL ^a	9.307
13	1	3.7	9.677
	2	UDL ^a	9.677

^a Under the detection limits.

The concentration of chromium released from the CS decreased by the extraction number. But, it was observed that the concentration increased again for the samples dried for 2 days. Chromium released also into solution above the limit concentration value of TCLP after seventh day or twelfth extraction. CS is mainly composed of collagen cross-linked with Cr(III) complexes. Increasing chromium concentration in further steps may be due to textural softening of the CS and decomposition of Cr(III) complexes. When taken into account of chromium contents of the CS and extraction solutions, it can be calculated that the 7.08% chromium in the CS released into solution after 12 extractions. This dissolution percentage seemed as small value causes important chromium pollution in water.

3.2. Stabilization of CS

The CS was heated under CO₂ atmosphere for the stabilization of chromium in it. In the preliminary experiments carried out at 500 °C, it was observed that a product mainly composed of carbon formed by heating of CS containing huge amount of organic compounds such as fats, peptides and amino acids. The product was subjected to dissolution experiments in order to test leachable concentration level of the chromium. The experimental results showed that the concentration of chromium released from the sample was under the detection limits and chromium was detained in the carbon structure. Since the thermal procedure applied is an expensive method, the experiments were carried out at the temperatures range of 250–500 °C for the temperature optimization. The thermal products obtained were also

Table 3
Chromium concentration released from the samples stabilized thermally

Stabilization temperature (°C)	Weight loss (%)	Released Cr concentration (mg/l)
250	12.59	7.69
300	37.06	1.65
350	48.95	UDL ^a
400	60.26	UDL ^a
500	62.40	UDL ^a
CS	–	9.27

^a Under the detection limits.

tested for the chromium dissolution. The results are presented in Table 3.

Chromium stabilization was not achieved for the CS heated up to 300 °C. While the concentrations of chromium released from the samples heated were above the maximum allowable concentration value of 5 mg/l, effective chromium immobilization was observed at the temperatures of 300 °C and above 300 °C. The concentrations of chromium leached out from the samples obtained at the temperatures above 300 °C were found to be below the detection limit, which is 0.5 mg/l. Although losses in weight of CS increased by heating, concentrations of the chromium released from the samples decreased. This situation shows that the chromium in the CS is stabilized by immobilizing in the carbonaceous material generated during the thermal operation. In order to clarify the immobilization mechanism, all samples were subjected to XRD analyses. But, it could not be detected any mineral formation. This situation may be attributed to the temperature and carbon dioxide atmosphere which is not an oxidative for the material. Tahiri et al. who have studied thermal behavior of CS and of sludges recovered after digestion of tanned solid wastes with calcium hydroxide have found similar results [11]. They have reported that the main crystallized phases such as chromium oxide (Cr₂O₃) and sodium chloride (NaCl) were obtained at 600 °C.

Consequently, it is stated that the thermal stabilization method applied to the CS is one of the best technique for the chromium immobilization. That the product (char) obtained by the thermal procedure can be solidified by mixing with asphalt and can be isolated from environment by using as a road pavement are also advantages.

3.3. TCLP test results

The toxicity characteristics leaching procedure (TCLP) [9] was applied to determine discharge situation of the CS and its products stabilized thermally.

TCLP tests results showed that the concentrations of chromium dissolved from the CS and the samples obtained at the temperatures of 250 and 300 °C were about 150, 77.2 and 6.15 mg/l, respectively, which were above the 5 mg/l limit for TCLP specified by USEPA. Therefore, it can be concluded that the CS-caused chromium pollution is a hazardous material for environment. However, effective stabilization of chromium in the CS was achieved by heating of CS at 350 °C (Table 4). The concentrations of chromium released from the products obtained

Table 4
TCLP test results

Sample	Released Cr concentration (mg/l)
CS	150.3
250 °C	77.2
300 °C	6.2
350 °C	UDL ^a
400 °C	UDL ^a
500 °C	UDL ^a
Allowable concentration value for Cr	5

^a Under the detection limits.

at the temperatures of 350 °C and above 350 °C were below the detection limits.

Depending on the results obtained from both dissolution experiments and TCLP test, it can be said that the chromium in the CS is stabilized by heating at 350 °C under the CO₂ atmosphere, the product stabilized is environmentally stable and it can be directly discharge.

4. Conclusion

Taking into consideration results obtained from this study where the leaching properties and pollution potential of the chromium in CS, which is a solid residue of leather industry, were investigated and thermal stabilization procedure was applied to the CS, the following conclusions may be drawn.

When the CS was contacted with water, the chromium in it released into water in the concentration above the maximum allowable concentration limit given as 5 mg/l by USEPA. It was determined that amount of the chromium dissolved increased with the increasing contact time and the decreasing liquid/solid ratio.

According to leaching experiments and TCLP tests results, it has been stated that the CS-caused chromium pollution is a hazardous material for environment.

Thermal stabilization process was applied to the CS due to its high organic compounds content. Effective stabilization of chromium in the CS was achieved by heating of CS at 350 °C under the CO₂ atmosphere. The sample stabilized was environmentally stable and thus it can be directly discharge. Also, it can be solidified by mixing with asphalt and can be isolated from environment by using as a road pavement.

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