

Processing of Used Leather Goods Containing Chromium VI and the Possibility of Detection of Chromium Traces by Raman Spectroscopy

KAREL KOLOMAZNIK*, MICHAELA BARINOVA, HANA VASKOVA

Tomas Bata University in Zlin
Faculty of Applied Informatics
Nad Stranemi 4511, 760 05, Zlin
CZECH REPUBLIC

*kolomaznik@fai.utb.cz, <http://www.fai.utb.cz>

Abstract: - In this paper, the authors deal with the problem of processing various types of waste generated by leather industry. Special emphasis is given to chrome tanned waste. The agent that makes this waste potentially hazardous is hexavalent chromium. Its compounds can have negative effects on human health and some chromium VI salts are considered carcinogens. The authors present the risks of spontaneous oxidation of trivalent chromium to its hexavalent form in various conditions, as well as an analytical method for detection of small concentrations of both forms of chromium using Raman spectroscopy. From the technological point of view, there are several ways of handling primary leather waste, but no satisfactory technology has been developed so far for the secondary waste (manipulation waste, e.g. leather scraps, and used leather products). In this contribution, a new technology of processing the secondary waste is presented and tested in industrial conditions. Commercial utilization of the products is discussed.

Key-Words: - Leather waste, recycling technology, hexavalent chromium, Raman spectroscopy

1 Introduction

Chrome-tanned wastes represent long-time threat not only to the environment, but also to the population health. The leather waste comprises:

- a) Tannery waste – liquid and solid (chromium splits, trims, shavings).
- b) Manipulation waste – e.g. leather scraps.
- c) Used leather goods (old shoes, upholstery, etc.).

Processing of the first group of wastes has been successfully solved and is described in several publications [1]. Another problem is manipulation waste generated during leather goods production, particularly footwear. Besides chromium, this waste also contains fillers, lubricants, dyes and synthetic resins, mainly polyurethanes and polyacrylates. We dealt with these wastes within the US-Asia Environmental Partnership program in Vietnam for the needs of the NIKE Inc. and the results were published e.g. in [2]. The last and still unsolved problem is the issue of used leather goods. This waste is usually a part of municipal waste and as such it is dumped or incinerated. However, relatively high chromium content makes this waste potentially hazardous. Its combustion produces besides nitrogen oxides also carcinogenic hexavalent chromium (Cr VI) compounds. Also disposal of this waste in landfills is related to the risk of uncontrolled oxidation of trivalent chromium (CrIII) to CrVI.

We have developed a hybrid technology that is able to process even the latter kind of waste. The key part of the

technology is mechanical separation of chrome-tanned collagen mass from the non-collagen additives.

Together with the development of the technology, our research is also focused on the precise detection of very low concentrations of CrVI not only in waste leather goods, but also in the still used ones. The analytical methods can also serve for determination of both CrII and CrVI concentrations in landfills or drinking waste sources where chromium can be washed out due to climatic conditions. Measuring only the total concentration of a particular element in environmental or clinical samples can often lead to errors in assessing toxicity, mobility, and bioavailability, as these effects can differ greatly between the various chemical species in which an element may occur [3]. Low concentrations of chromium were measured in [3] with the use of inductively coupled plasma mass spectrometry (ICP-MS) coupled to a liquid chromatography (LC) system in mineral water. The authors of [4] detected CrVI and CrIII concentrations in sea water by flame atomic-absorption spectrometry. This method was also recommended for determination of CrVI and CrIII in tannery effluents. In [5] is described a method for detection of CrVI compounds in air and at workplaces by differential pulse polarography (DPP). A differential pulse polarographic method was also used for detection of CrVI in environmental and soil samples [6]. Kikuchi et al. [7] in their paper reported the ability of distinguishing CrIII from CrVI with the use of Raman

spectroscopy in electrical and electronic equipment. The Raman spectroscopy so far seems a promising method to detect CrVI in samples of various natures. For this reason, we are working at development of a precise analytical method of CrVI detection with the use of Raman spectroscopy. In this contribution we deal with an innovative technology of processing used leather goods including the possibilities of industrial application of the products. We also present preliminary results from detection of CrVI in leather samples with the use of Raman spectroscopy.

2 Theory

2.1. Spontaneous oxidation of CrIII to CrVI

Compounds of CrVI are easily absorbed into the body through the skin [8]. They can cause dermatitis, often connected with lesions [9]. The greatest risk, however, lies in the fact that reactions of CrVI compounds with cell membranes can lead to kidney and urinary tract carcinomas [8, 10]. The publication [11] also points out an alarming increase in oncological diseases of kidney and urinary tract in the Czech Republic, which may be connected with wearing shoes on bare feet and the increasing import of relatively cheap footwear to the country. The basic question is the possible oxidation reaction from CrIII to CrVI. In basic solutions, the oxidation of CrIII to CrVI by oxidants such as peroxides and hypohalide occurs with ease [8]. Such strong oxidation conditions are realized in the process of the sterilization of drinking water. Another problem concerns the possibility of oxidation of CrIII into CrVI in gentle conditions by air in the wide range of pH:



in alkali medium, and



for acid medium.

The published thermodynamics functions (Gibbs energies of formation) are shown in Table 1 [12]:

Table 1 Gibbs free energy of reaction components.

Reaction Component	Change of Gibbs free Energy ΔG (kJ.mol ⁻¹)
Cr ₂ O ₃	-1053.00
OH ⁻	-157.28
O ₂	0.00
CrO ₄ ²⁻	-727.85
H ₂ O	-228.61
Cr ₂ O ₇ ²⁻	-1301.20
H ⁺	0.00

Spontaneous oxidation of CrIII into CrVI is possible within a wide range of pH as shown by the Gibbs Energy values for both reactions:

$$\Delta G_f^0 = -4 \times 727.85 - 4 \times 228.61 - (2 \times 1053 - 8 \times 157.28) = -459 \text{ kJ}$$

for alkali medium and

$$G_f^0 = -2 \times 1301.2 - (2 \times 1053 - 2 \times 228.61) = -22.12 \text{ kJ}$$

for acid medium.

The negative values of both thermodynamic functions prove the possibility of spontaneous oxidation within a wide range of pH. This fact is more dangerous than in the previous case because we do not know under which conditions CrIII may be converted into CrVI.

2.2. Raman spectroscopy

Raman spectroscopy has recently proved progressive benefits and become an effective research technique which finds applications across the science disciplines. Prime advantages as non-destructiveness, rapidity, contactless measurements or no special requirements for sample preparation makes this method attractive, convenient and effective. Raman spectroscopy also grants highly specific chemical “fingerprint”. Every single chemical element, its modification or chemical compound gives rise to a different and unique Raman spectrum – the key for the identification.

The basic principle of Raman spectroscopy is depicted in the following Figure 1 [13]:

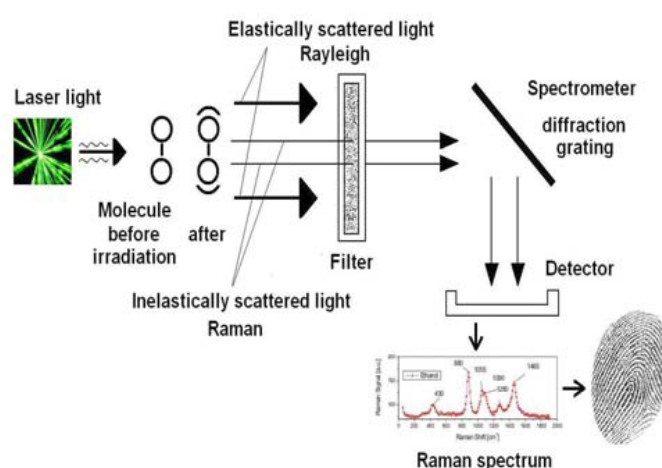


Fig. 1. The sample is irradiated with laser, molecule vibrato, filter eliminates intense Rayleigh scattering, and the grating disperses the light onto a detector to generate a spectrum, which gives the information about molecule bonding.

3 Experimental

3.1. Determination of Cr spectra in leather sample

A sample of chrome-tanned leather was merged into a solution of chromium bichromate to contain both forms of chromium. Raman spectra of leather containing chromium compounds were recorded using Renishaw InVia Basis Raman microscope equipped with two lasers: argon ion laser with the excitation wavelength 514 nm and laser maximum output power of 20mW and near-IR diode laser with the excitation wavelength 875nm and laser maximum output power of 300mW. Leica DM 2500 confocal microscope with the resolution up to 2 μ m was coupled to the Raman spectrometer.

3.2. Industrial tests of the processing technology

We carried out industrial scale trial using Nike leather scraps as the input raw material. This technology is also suitable for the processing of used leather goods, especially old shoes, with the preceding separation of leather and synthetic part. The separated parts are subsequently subjected to mechanical crushing to facilitate their further processing. The leather part is then treated according to the following scheme (Table 2):

Table 2 Course of the industrial trial.

Destruction of surface resins
Alkaline saponification of fats
Neutralization
Enzymatic hydrolysis at pH 9 catalyzed by ALCALASE DX-L
Neutralization at pH 5.7
Converting emulsion to a suspension
Careful filtration (critical step)
Separation of protein solution from hydrated chromium and titanium hydroxides

A stirring reactor with total load capacity 17 tons of reaction mixture was used. The batch of reaction mixture was the following: 300 kg of NLS (Nike Leather Scrap), 60 kg of pure potassium hydroxide and 5,940 kg of technological water (without chlorine). The industrial trial was carried out in the KORTAN Company in Hradek nad Nisou, Czech Republic.

4 Results and discussion

The first part of our paper deals with the still topical need for economical and environmentally friendly processing of chrome tanned leather waste. We particularly focus on manipulation waste generated during processing leather into the final products of leather industry and used leather goods such as old shoes. For these wastes, we have proposed and

industrially tested a hybrid technology. The industrial tests gave the following products:

5,500 kg of filtrate with dry matter content 4.5% and 900 kg of filter cake. The filter cake was freely dried and the filtrate was concentrated in the vacuum evaporator to the dry matter content of 22%. The concentrated protein hydrolyzate (NPK – organic fertilizer) was dried in the fluidization dryer and 130 kg of dry hydrolyzate was obtained. Especially the filtrate seems to be economically very interesting. Due to the addition of potassium hydroxide and phosphoric acid during the hybrid process, the concentrated and dried filtrate represents a good quality NPK fertilizer.

In addition to the manipulation waste, the hybrid technology seems to be an effective solution also for used leather products, e.g. old shoes. These goods, especially those in which the chromium content is not carefully controlled, represent potentially hazardous waste in the same way like chrome shavings or leather scraps and should not end up in municipal waste. The authors propose selective collection (like it is already done with paper, plastics, glass and metals) of these used products. After crushing, the hydrolysable parts can be processed by the above mentioned hybrid technology. The processing of the other part, which cannot be hydrolyzed, is a subject of intensive research. According to preliminary results, pyrolysis of the non-collagen parts seems to be an effective way, with a focus on products applicable as liquid fuels.

The other part of the paper is focused on detection of CrIII and CrVI, especially in leather samples. The following Figure 3 shows the Raman spectra of trivalent and hexavalent chromium.

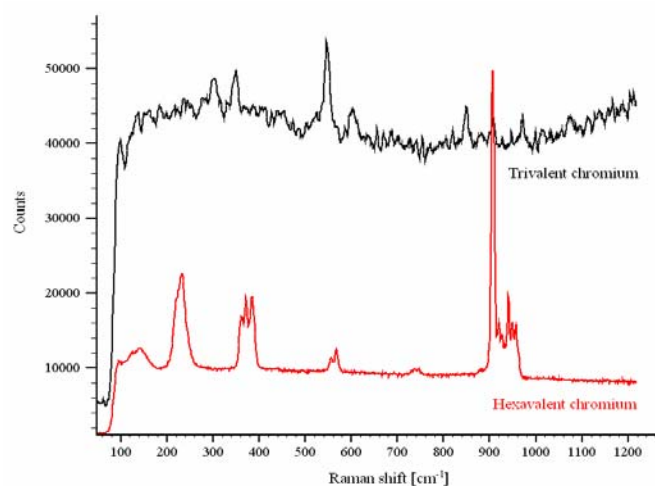


Fig. 3. Raman spectra of trivalent and hexavalent chromium in leather sample.

The spectra of both forms show obvious differences. The figure also implies complication with luminescence of

the leather when using visible light Ar⁺ laser. More suitable for detecting chromium compounds in leather is less energetic near infrared laser which provides much better and clearer spectra. We have recently obtained such laser in our laboratory and in the near future we will publish the first results. The essential fact is that Raman spectroscopy can be used for the evaluation of the presence of chromium compounds in leather.

There are very few reports on analytical methods for the detection of CrVI traces in leather samples, especially used leather goods, or the behavior of chromium compounds in various conditions (e.g. the micro-environment in the contact area of a bare foot and footwear). Some attempts have been published in [18], where automobile leather samples were artificially aged by using UV radiation and/or temperature aging factors. The alteration of leather structure was investigated by Raman Spectroscopy. Increase of CrVI and formaldehyde contents and decrease of chromic oxide and soluble matter in dichloromethane contents were determined in finished automobile leather samples after the ageing process. This supports our theory that used leather goods represent a potential threat to its users and the environment, especially when directly exposed to climatic conditions. In the near future, we plan to develop a more precise analytical method for the detection of very low CrIII and CrVI concentrations to determine the conditions for the prevention of spontaneous oxidation.

5 Conclusion

Possibility of spontaneous oxidation of CrIII present in leather wastes and goods to CrVI is discussed. Preliminary results are presented from analytical detection of low concentrations of chromium in leather samples using Raman spectroscopy. A new three-step hybrid technology of processing manipulation waste is proposed and tested under industrial conditions. The filtrate obtained by this technology can be used in agriculture as a good quality NP or NPK fertilizer. The solid product can serve as an inorganic pigment in glass and ceramic industry. The technology also seems to be an effective solution for hydrolysable parts of used leather products, e.g. old shoes.

Acknowledgements:

This work was supported by research project MSM 7088352102 and ERDF Project CEBIA Tech No. CZ.1.05/2.1.00/03.0089. This support is very gratefully acknowledged.

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