



Leather waste—Potential threat to human health, and a new technology of its treatment

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ARTICLE INFO

Article history:

Received 22 September 2007

Received in revised form 6 March 2008

Accepted 6 March 2008

Available online 22 March 2008

Keywords:

Leather waste

Hexavalent chromium

ABSTRACT

In this paper, the authors deal with the problem of processing various types of waste generated by leather industry, with special emphasis 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 CrVI salts are considered carcinogens. The authors present the risks of spontaneous oxidization of CrIII to CrVI in the open-air dumps as well as the possible risks of wearing bad quality shoes, in which the chromium content is not controlled. There are several ways of handling primary leather waste, but no satisfactory technology has been developed for the secondary waste (manipulation waste, e.g. leather scraps and used leather products). In this contribution, a new three-step hybrid technology of processing manipulation waste is presented and tested under laboratory, pilot-scale and industrial conditions. The filtrate can be used as a good quality NPK fertilizer. The solid product, titanium–chromium sludge, can serve as an inorganic pigment in glass and ceramic industry. Further, the authors propose selective collection of used leather products (e.g. old shoes), the hydrolysable parts of which can be also processed by the new hybrid technology.

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1. Introduction

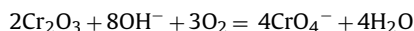
People use products of the leather-processing industry on a daily basis. These include especially shoes, leather and textile goods; we normally encounter leather products even in both public and private transport. The primary raw material for final products is hide from animals from slaughter houses and hide from game—i.e. waste from the meat industry, which is processed in tanneries and turned into leather. Therefore, the tanning industry can be considered one of the first industries to use and recycle secondary raw materials.

Although the tanning industry is environmentally important as a principal user of meat industry waste, the industry is perceived as a consumer of resources and a producer of pollutants. Processing one metric ton of raw hide generates 200 kg of final leather product (containing 3 kg of chromium), 250 kg of non-tanned solid waste, 200 kg of tanned waste (containing 3 kg of chromium), and 50,000 kg of wastewater (containing 5 kg of chromium) [1]. Thus, only 20% of the raw material is converted into leather, and more than 60% of the chromium is in the solid and liquid waste.

During the production of leather goods, especially shoes, manipulation waste is produced, which makes about 15–20% of the entry material—leather. The last kinds of waste are used leather products which have lost their utility value.

1.1. The possibility of oxidation of CrIII to CrVI

The basic question is the possible oxidation reaction from chromium III to chromium VI. In basic solutions, the oxidation of CrIII to CrVI by oxidants such as peroxides and hypohalide occurs with ease [2]. Such strong oxidation conditions are realized in the process of the sterilization of drinking water. This is the first threat to human health and life. Rain (especially acid rain) can leach chromium III from waste dumps, and soluble salts can then reach sources of drinking water. During the sterilization process by ozone or hypochloride, chromium III is converted into chromium VI and reacts with magnesium and calcium ions occurring in drinking water to produce carcinogenic magnesium and calcium chromate or dichromate salts. Another problem concerns the possibility of oxidation of CrIII into CrVI in gentle conditions by air in the wide range of pH. Principally, oxidation can be realized after the following equations:

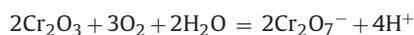


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Table 1
Gibbs free energy of reaction components [3]

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

in alkali medium, and



for acid medium.

The probability of a spontaneous oxidizing process of CrIII into CrVI is real as the Gibbs energy values for both reactions show. The published thermodynamics functions (Gibbs energies of formation) are shown in Table 1:

We calculated Gibbs energy for both reactions:

$$\begin{aligned} \Delta G^0 &= -4 \times 727.85 - 4 \times 228.61 - (2 \times 1053 - 8 \times 157.28) \\ &= -459 \text{ kJ} \end{aligned}$$

for alkali medium and

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

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. It is a question of the kinetics of the above-mentioned reactions.

Leather and leather products may sometimes contain traces of hazardous CrVI, although only CrIII compounds are used in the tanning process. There are some possible sources for the occurrence of CrVI in the leather-tanning process. CrVI may possibly be present as a contaminant in the tanning agent. Fat-liquoring with unsaturated fatty acids and fish oils may, after photo-ageing with UV light or thermal treatment (dry heating over 80 °C), possibly lead to the oxidation of CrIII. Storage of fat-liquored leather at a relative humidity above 35% may result in CrVI formation. Use of alkaline glues in shoe production may also provoke the formation of CrVI.

1.2. Potential dangers of hexavalent chromium in connection with leather goods

CrIII and CrVI compounds are produced in large quantities and are accessible to most of the population. The primary routes of entry for animal exposure to chromium compounds are inhalation, ingestion, and for hexavalent compounds skin penetration. This last route is the most significant. Most hexavalent chromium compounds are readily by skin, are more easily soluble than trivalent chromium in the pH range 5–7, and react with cell membranes. The target organ for acute systematic toxicity is the kidney. Usually, poisoning by CrVI results in acute tubular necrosis of the kidney, a reported cause of death [2]. Prolonged contact with certain chromium components may produce allergic reactions and dermatitis in individuals [2]. There is evidence that hexavalent chromium may be carcinogenic. The National Institute for Occupational Safety and Health has classified the chromate and dichromate salts of calcium and magnesium (elements occurring in soil and drinking water) as carcinogenic compounds [2]. The key to the hexavalent chromium's mutagenicity and possible carcinogenicity is the ability of this oxidation state to penetrate the cell membrane.

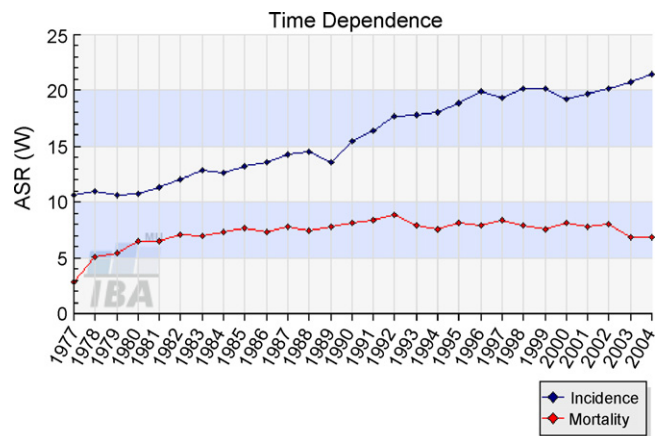


Fig. 1. Time development of mortality rate and incidence in the urinary bladder (men).

There is another aspect of CrVI that may have both health and environmental impact. Although only minor attention has been paid to this problem so far, there is increasing evidence that in the near future this problem should be taken into account. As it has already been mentioned above, one of the potential entrances of CrVI into human body is skin penetration. This may possibly happen, for example, when wearing shoes on bare feet. Usually, shoe production is under strict control, but a considerable amount of shoes has been imported within the last two decades from countries in which the chromium content is not always carefully monitored, and this import is rapidly increasing (see Figs. 7 and 8). These shoes thus represent not only a potential threat to the users, but also become an environmental issue when worn out and dumped in the open air.

As a reported carcinogen affecting kidney and urinary tract [2], CrVI can be possibly connected with some cases of neoplasms. The fact that malignant tumours of these organs may be caused by CrVI compounds is also pointed out in literature [4,5]. This, together with a potential entrance of CrVI into human body through skin, makes a combination that should not be ignored.

The following figures (Figs. 1–6) [5], presented with kind permission of the Institute of Health Information and Statistics of the Czech Republic, show time developments of the incidence of kidney, renal pelvis and urinary bladder neoplasms. The symbol ASR – age standardized rate – in the y-axis of the figures means a summary measure of a rate that a population would have if it had a

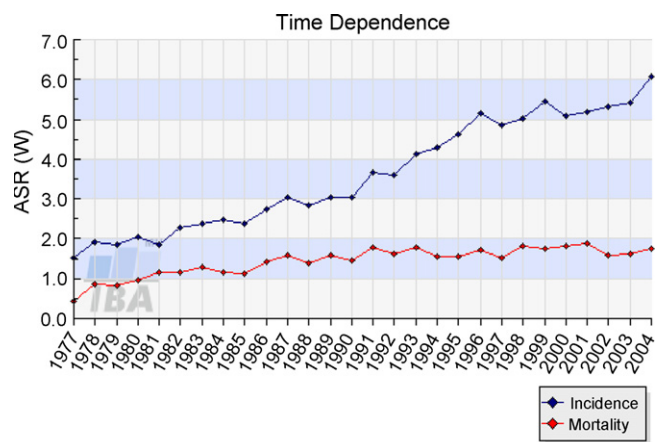


Fig. 2. Time development of mortality rate and incidence in the urinary bladder (women).

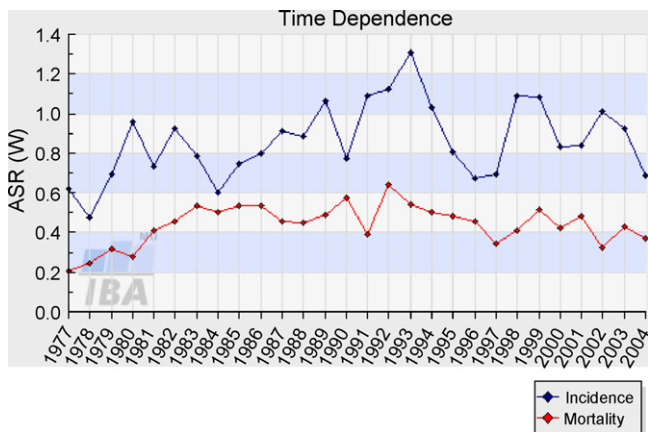


Fig. 3. Time development of mortality rate and incidence in the renal pelvis (men).

standard age structure. Standardization is necessary when comparing several populations that differ with respect to age because age has such a powerful influence on the risk of cancer. The symbol (W) expresses that the numbers have been adjusted to the World Standardized incidence rate. It is expressed per 100,000 persons.

The following Figs. 7 and 8 show the overview of footwear production, import and consumption during the last two decades in the USA and the Czech Republic, respectively.

It is interesting to compare the percentage growth in the number of neoplasms in the urinary bladder, the kidney excluding the renal pelvis, and the renal pelvis. As shown in Figs. 1–6, the growth is two to three times higher in women than men. One of the possible explanations might be the fact that women use socks 10 times less often, while socks act as a barrier against the sorption of trace amount of hexavalent chromium from leather by the skin surface.

2. A new technology for processing secondary waste from leather industry

2.1. Existing solutions of waste disposal in the tanning industry

2.1.1. Waste dumps

The simplest solution is to put the waste from the leather-processing industry on waste dumps. For example, in the Czech Republic, over 1.5 million tonnes of chrome-tanned waste is stored on various dumping sites. Considering the danger of leaching of chromium salts by acid rain, with a potential danger of leakage into

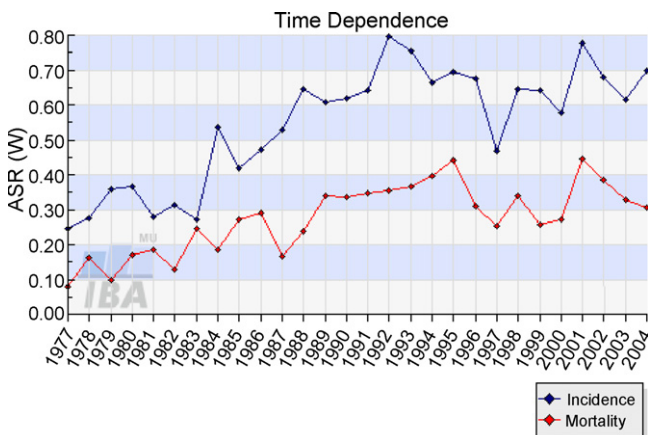


Fig. 4. Time development of mortality rate and incidence in the renal pelvis (women).

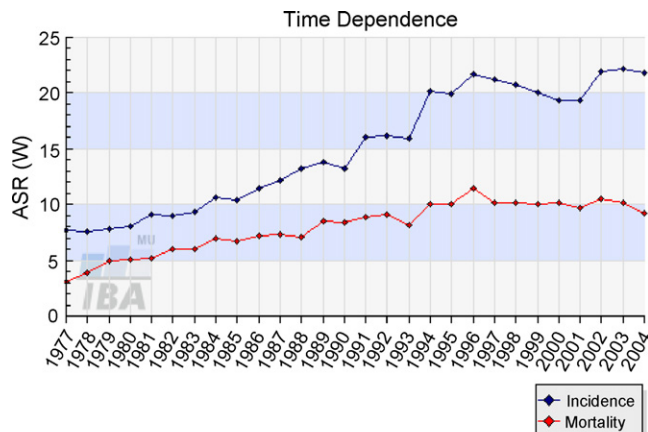


Fig. 5. Time development of mortality and incidence in the kidney, excluding the renal pelvis (men).

drinking water sources and subsequent oxidation of CrIII into CrVI during disinfection, this solution is the least suitable from the point of view of environmental protection.

2.1.2. Combustion

An advantage of combustion of chrome-tanned waste from the tanning industry is the relatively high content of organic base which produces heat in the process of combustion. A disadvantage is the total oxidation of trivalent chromium into hexavalent chromium, whose calcium chromate is a carcinogenic compound. The issues of combusting chrome-tanned wastes are also pointed out in [8]. A perfect separation of combustion gasses and ash is necessary as well as a safe disposal of the ashes as a highly hazardous waste. It is also necessary to pay attention to the increased content of nitrogen oxides which is created during the combustion of collagen proteins.

2.1.3. Pyrolysis or carbonization

High-temperature decomposition of chrome-tanned wastes that produces chrome green of high quality is at present intensely researched. However, practical industrial implementation has not been carried out yet.

2.1.4. Chemical treatment

There are basically two possible ways of chemical treatment of chrome shavings—by oxidation or hydrolyses. In the oxidation

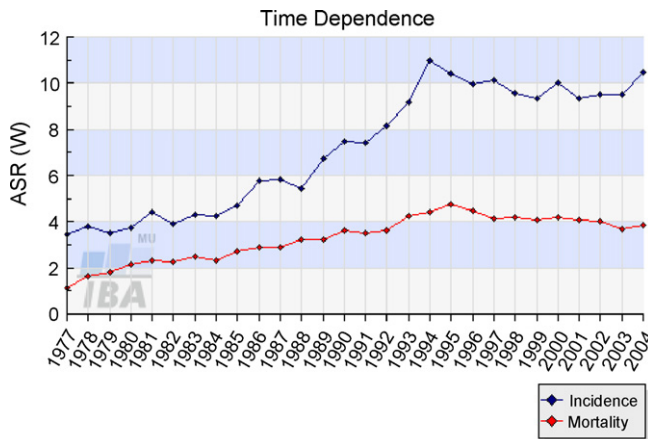


Fig. 6. Time development of mortality and incidence in the kidney, excluding the renal pelvis (women).

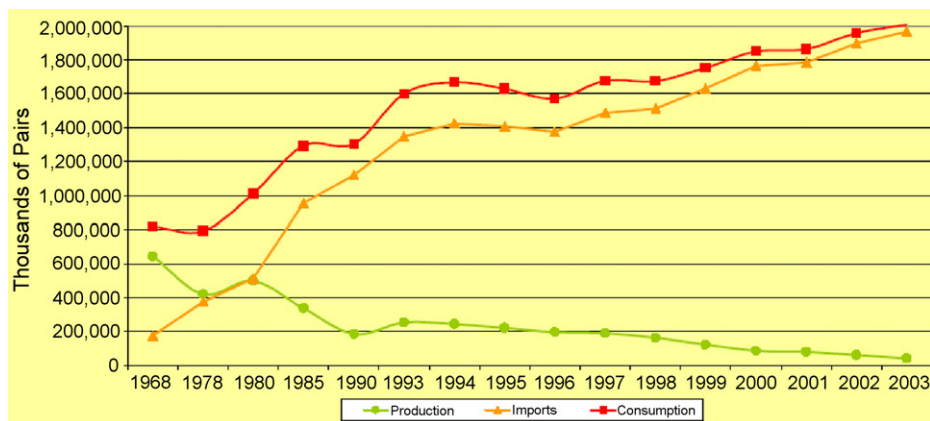


Fig. 7. The overview of footwear import in the USA in the years 1990–2004 [6].

process, in alkaline conditions, chromium salt is liquidized by oxidation by hydrogen peroxide, and the chromate that is created is leached from the heterogenic reaction compound by water. The main disadvantage of this method, apart from the above-mentioned creation of carcinogenic chromium salt, is also the production of a considerable amount of diluted solutions of chromium salt, which makes the process non-economical. However, an advantage is a high-quality gelling protein with high bloom value. Hydrolysis of chrome-tanned wastes in acid or alkaline conditions is more environmentally friendly as no hexavalent chromium is created due to the reaction time.

One of the numerous possible solutions to the problem of chrome-tanned wastes is their enzymatic digestion which has been dealt with in detail in a number of publications [9–12]. When researching processing of chrome-tanned wastes in the Czech Republic, we decided to utilize the enzymatic dechromation technology worked out at the USDA in Philadelphia [13]. The technology was adapted to conditions in a factory that manufactures auxiliary tanning agents. Furthermore, we modified the American process by using volatile organic bases such as isopropylamine, diisopropylamine, cyclohexylamine, ammonia, and others. The use of volatile amines produces higher quality of protein hydrolysates and chromium sludge.

2.1.5. Direct application of solid tannery waste

Due to a relatively large specific surface of solid tannery waste (approximately $10\text{ m}^2\text{ g}^{-1}$ [14]) it is possible to use this waste for decontamination of textile industry wastewater, which contains organic dyes. This method has been proposed in [15] to remove methylene blue and reactive red textile dye from aqueous residues.

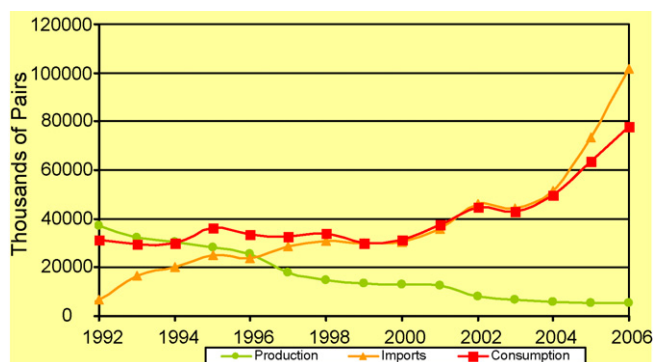


Fig. 8. The overview of footwear import in the Czech Republic in the years 1990–2006 [7].

High sorption capacity of solid tannery waste (80 and 163 mg g^{-1} for methylene blue and red textile dye, respectively) makes this method an interesting alternative to commercial adsorbent materials.

Another promising application of solid tannery waste has been published in [16]—the waste serves as an adsorbent for removal of toxic Cr(VI) and As(V) from aqueous media. The sorption capacity is described by Langmuir and Freundlich isotherms. The amount of adsorbed Cr(V) and As(V) (133 and 26 mg g^{-1} , respectively) shows a great potential for future use. The sorption capacity of tannery waste (chrome shavings) has been also used in [17] for removal of motor oils, other oily waste and hydrocarbons from water. The shavings are capable of adsorbing approximately seven times their weight in oils and hydrocarbons.

2.2. Processing manipulations waste and used leather goods

However, the chemical procedures elaborated for processing primary wastes fail in case of secondary wastes from the production of leather products, especially shoes. The presence of chromium six in worn shoes was brought up in [18]; more than 90% of leather goods are tanned with alkaline chromium salts [19]. We were looking for the solution to this problem in cooperation with USDA, ERRC, Wyndmoor USA and the Texas Technical University in Lubbock for manipulation wastes in the NIKE Company. We elaborated a hybrid technology in three steps. In the first step, synthetic resin (polyurethane and polyacrylate) is decomposed in a strongly alkaline environment of potassium hydroxide ($\text{pH} \sim 12$) resulting in a strongly stable emulsion, which cannot be broken up due to the stabilization by hydrolysing products. In the second step, after adjustment to $\text{pH} \sim 9$ by phosphoric acid, a proteolytic enzyme is dosed and enzymatic hydrolysis is carried out, decreasing the molecular weight from the original 100–10 kDa. In the last step, pH is adjusted again to the neutral level 7 and the resulting suspension is relatively easy to filtrate. The filtrate is vacuum-evaporated to 20–40% solid matter content and used as NK (nitrogen–potassium) or NPK (nitrogen–phosphorus–potassium)—organic fertilizer. The titanium–chromium sludge can be used as inorganic pigment in glass or ceramic industry.

Used leather products, especially old shoes, are at present most often taken to waste dumps together with communal waste or burnt, which is, as we have shown, not an ideal solution. Much more suitable is selective collection of used leather goods, just as in the case of used paper, plastics, glass and metal. This solution would enable separate processing especially of the chrome-tanned wastes.

Table 2
The individual steps of the laboratory experiment

Time (min)	Temperature (°C)	pH	Note
0	70		
50	70	11.9	
180	70	11.6	
185	70	9.0	Add 2 ml 15% HNO ₃
190	70	9.0	Add 5 ml 0.1% Alcalase
380	70	9.1	End

3. Experimental part

3.1. Laboratory experiments

The main goal of the experimental part was presented hybrid technology for its industrial implementation. First, we carried out a number of laboratory experiments, the results of which are shown in Tables 2–4. Also, we carried out a pre-production test and a production test. The entry raw material in these tests was manipulation waste from the NIKE Company.

In the first run, 5 g of milled leather scraps was put into the reaction vessel, and 100 ml of 1% potassium hydroxide solution was added. After 3 h of alkali pre-treatment at 70 °C with stirring, the pH value of the mixture in the reaction vessel was adjusted to value 8.8 and 9.4 with 15% solution of nitrite acid (phosphoric acid may be used, too).

In the second run, 0.1% solution of commercial enzyme alcalase was added. The amount of the added alcalase influences the effectiveness of decomposition process. After 2 h of enzymatic hydrolysis at 70 °C with stirring the reaction solution was filtered.

Hydrolysate as a water-soluble peptide mixture and an insoluble chromium cake were filtration products. The hydrolysate was analysed for the total solid matter, total ash, nitrogen, chromium and titanium content. The chromium cake was analysed for total solid, total ash and nitrogen content.

Total solid matter content was determined by heating the samples at 105 °C, nitrogen content according to Kjeldahl method (TNK, total Kjeldahl nitrogen), total ash content by burning the sample at 800 °C in Muffle furnace. Chromium content was determined by atomic absorption spectroscopy using GBC 933 AA instrument (GBC Scientific Equipment Pty Ltd., Dandenong, Victoria, Australia). Titanium content was determined by atomic absorption spectroscopy using GBC GF 3000 instrument (GBC Scientific Equipment Pty Ltd., Dandenong, Victoria, Australia).

Table 3
Mass balance of the laboratory experiment

Total quantity	Dry matter content (%)
Filter cake 21.16 g	13.32
Filtrate 74 ml	3.71
Total mass difference	10.2
Balance of dry matter difference	4.9

Table 4
Analysis of the filtrate (hydrolysate) and filtration cake (FK) obtained from the laboratory experiment

	Total solid	Total ash ^a (%)	Nitrogen ^a (%)	Cr ^a ppm in FK (%)	Ti ^a ppm in FK (%)
Hydrolysate	5.6	29.2	9.8	309	31
FK	24.1	38.5	5.3	24.6	11.7

^a On the free moisture base.

Table 5
The course of the semi-pilot experiment

Time (min)	Temperature (°C)	pH	Note
0	70	13.59	
60	70		Foam
85	70	11.5	
120	70	11.19	
180	70	11.18	
240	70	10.85	
			+10 g of solid KOH
		11.43	To 500 ml H ₂ O
360	70	–	Foam
420	70	–	Stopped during the night
1440	70	–	Continue next day
1530	70	10.53	
			+10 g of solid KOH
		11.01	To 250 ml H ₂ O
1710	70	10.92	
		9.32	+27.5 ml 65% HNO ₃
			+0.5 g 100% alcalase
1860	70	9.33	Stopped during the weekend
3300	70		Continue next day
3345	70	9.19	
3405	70	7.31	+25 ml 65% HNO ₃
			Neutralization
3465			End

3.2. Semi-pilot experiment

We used 1 kg of leather scrap so that the propeller of the stirrer was absolutely immersed into the reaction mixture consisting of leather scraps and 10 kg of 1% water solution of potassium hydroxide. The individual steps of the semi-pilot experiment are described in Table 5; Table 6 shows the mass balance of the experiment.

Load of the washing machine:

1000 g of leather pieces,
10,000 g of 1% water solution KOH.

Enzymatic hydrolysate solution was dried in open air at the average temperature of surrounding air 20 °C and moisture 50%. Drying in these conditions took 70 h. The filter cake was dried in the same way.

3.3. The record of the industrial trial course

For the hybrid technology of protein hydrolysate preparation, the stirring reactor with total load capacity 17 tonnes of reaction mixture was used. In the first step, the destruction of surface synthetic resins and the alkaline saponification of present fats were realized. After the neutralization, the enzymatic hydrolysis at pH 9 with catalysis of industrial proteolytic enzyme ALCALASE DX-L (producer Novo-Nordisk Denmark) was carried out. After the enzymatic hydrolysis was finished, the neutralization of reaction blend (pH 5.7) was carried out, and the emulsion of the reaction mixture was transformed into suspension. The above-mentioned operation is one of the key steps because its result influences the successful separation of protein solution from the precipita-

Table 6
Mass balance of the semi-pilot experiment

Filter cake 1.429 g	Dry matter content 32.09%
Hydrolysate 7.500 ml	Dry matter content 8%
Total mass difference	2%
Balance difference of dry matter	24%

Table 7
The course of the industrial experiment

Total time (h)	Temperature (°C)	pH	Note
0	12	6.4	Loading of 5940 kg water
0.58	12	6.4	Beginning of KOH dissolving
0.75	15	14	End of KOH dissolving
0.83	15	–	Beginning of 300 kg NLS dosing
1	15	–	End of 300 kg NLS dosing
1.25	15	–	Beginning of reactor heating
2.75	70	12	Optimum temperature achievement
5.75	69	–	Addition of 30 kg HNO ₃ 65% p.a.
5.9	73	9.9	Addition of 5 kg HNO ₃ 65% p.a.
6	74	8.94	–
6.1	74	8.9	Addition of 2.5 kg ALCALASE enzyme
7	73	8.9	Test of filtration—very slow
9	72	–	Stopping of steam supply
10	70	–	Stopping of stirring
	The reaction continued the next day		
23	57	6.5	Gradual addition of 19 kg phosphoric acid p.a. 85%
24	65	6.5	Taking of 400 kg heterogeneous reaction mixture on filter
26	70	6.5	End of 400 kg heterogeneous mixture filtration
26.5	70	5.73	Gradual addition of 3 kg HNO ₃ 60% p.a.
27	68	5.73	Gradual filtration (four times) nest 3700 kg of mixture
34	65	5.73	
35	61	5.73	Gravimetric filtration during the night. Filtration of 2200 kg mixture

tions of hydrated chromium hydroxide and titanium hydroxide [Cr(OH)₃ × H₂O; Ti(OH)₂ × H₂O]. Hence, we proceeded very carefully and the rate of filtration was determined on a laboratory scale. The following Table 7 provides the information about the hydrolysis process. The industrial trial was carried out in the KORTAN Company in Hradek nad Nisou, northern Bohemia (see Figs. 9 and 10).

The batch of reaction mixture:

300 kg of NLS (Nike Leather Scrap),
60 kg of pure potassium hydroxide,
5940 kg of technological water (without chlorine).

By filtration, we obtained 5500 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 hydrolysate (NPK, organic fertilizer) was dried in the fluidization dryer and 130 kg of dry hydrolysate was obtained.



Fig. 9. Part of the device for the industrial trial (KORTAN Company, Hradek nad Nisou).



Fig. 10. Stirring of the filtrate during the industrial trial (KORTAN Company, Hradek nad Nisou).

4. Discussion

In the first part of our study we focus on the health and environmental risks of hexavalent chromium compounds. These compounds can be created by spontaneous oxidation of Cr(III), which is commonly present in chrome-tanned leather goods and, consequently, chrome-tanned leather waste. Shoes, a widely used type of leather goods made predominantly of Cr(III) tanned leather (but traces of Cr(VI) can be also present there), can represent a combination of both health and environmental risks. As there is evidence in literature of skin penetration of Cr(VI) compounds [2], there is a strong possibility that Cr(VI) can directly affect humans when wearing shoes, especially on bare feet. However, it is necessary to carry out a detailed research into the conditions in which Cr(III) is transformed to Cr(VI), i.e. to solve a kinetic question. It is already known that temperature, moisture, UV radiation and alkaline conditions can accelerate the above-mentioned transformation [20].

In order to prevent health risks, several legislative regulations have been issued, limiting the Cr(VI) content in leather products to the maximum of 2–10 mg kg⁻¹, while for eco-labelled leather, the

CrVI concentration should not exceed 0.5 mg kg^{-1} . To comply with these legislative requirements, reliable measurement of CrVI content in leather is of extreme importance. However, with increasing shoe import in the last few decades, it seems that CrVI health threat should be again taken into account. The imported shoes do not always comply with the required quality and chromium content is not always carefully monitored. In our study, we particularly point out the possible connection between CrVI and some types of cancer. The goal of that part of our paper is to show that the role of CrVI as carcinogen cannot be neglected, and when there is an increasing incidence of some kinds of cancer, it is necessary to count all the possible causes.

The second 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. As there has not been developed a satisfactory technology for manipulation waste so far, this paper represents a pilot study in this field. We have proposed and industrially tested a hybrid three-step technology, the products of which can be applied in agriculture and ceramic industry. 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 the semi-pilot testing, the dried filter cake containing chromium oxide, titanium oxide (Cr_2O_3 and TiO_2) (in the case of NIKE Company) and organic residue was tested for dyeing of enamel in Vietnam with promising results.

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.

5. Conclusions

This study concerns the potential health risks of hexavalent chromium in the waste generated by leather industry and the possibilities of economical and environmentally friendly processing of this waste. Special attention is given to so-called secondary waste, i.e. manipulation waste generated during processing leather into the final products of leather industry and used leather goods. A new three-step hybrid technology of processing manipulation waste is presented and tested under laboratory, pilot-scale and 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. For this reason, the authors propose selective collection of this kind of waste.

Acknowledgements

The project was financed by the Ministry of Education of the Czech Republic, VZ MSM 7088352102.

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